

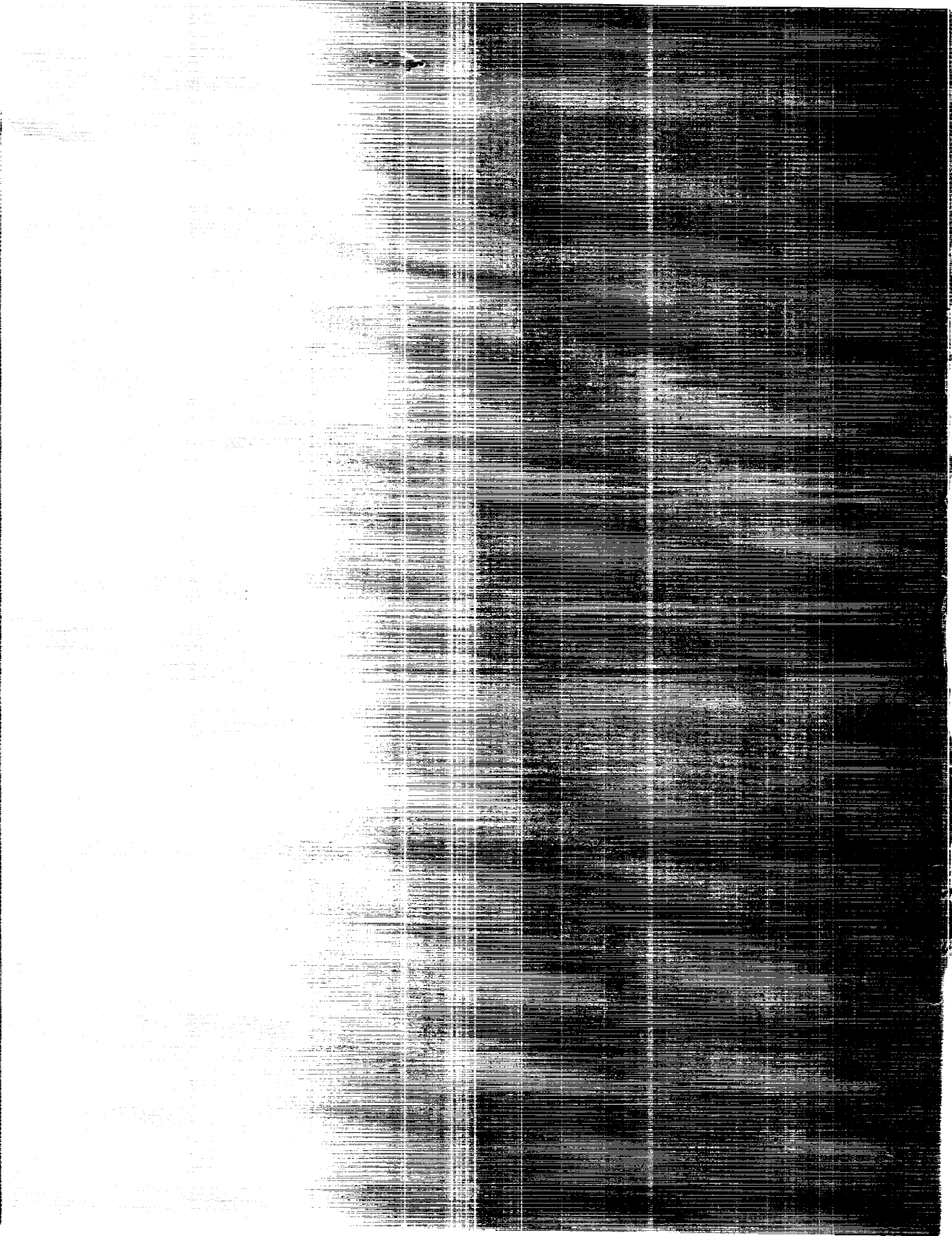
Thermodynamic Chemical Stability of Materials in Hydrogen Atmospheres

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CHEMICAL STABILITY OF CERAMIC MATERIALS IN
HYDROGEN-CONTAINING ATMOSPHERES AT HIGH
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Thermodynamic Analysis of Chemical Stability of Ceramic Materials in Hydrogen-Containing Atmospheres at High Temperatures

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Summary

The chemical stability of several ceramic materials in hydrogen-containing environments has been analyzed from thermodynamic considerations. Equilibrium calculations were made as a function of temperature, moisture content, and total system pressure. The following ceramic materials were considered in this study: SiC, Si₃N₄, SiO₂, Al₂O₃, mullite, ZrO₂, Y₂O₃, CaO, MgO, BeO, TiB₂, TiC, HfC, and ZrC. On the basis of purely thermodynamic arguments, upper temperature limits are suggested for each material for long-term use in H₂-containing atmospheres.

Introduction

Structural ceramics and ceramic composites are prime candidates for use in the hot section of advanced high-temperature propulsion systems for future aerospace applications. Hydrogen is being considered as a fuel for many of the advanced propulsion systems. A few examples of such systems are the Stirling engine, the advanced Earth-to-orbit propulsion (ETOP) systems, and the national aerospace plane (NASP). With hydrogen as the fuel, the hot section environment for all of these applications is likely to range from pure hydrogen to hydrogen plus moisture.

The potential use of ceramic components in these advanced propulsion systems would be dictated by the chemical stability of the ceramic materials in hydrogen-containing environments at elevated temperatures. A comparison of the stability of different ceramic materials in H₂-containing environments, based on thermochemical analysis, is useful for screening different candidate ceramic materials. Multicomponent equilibrium calculations based on the principle of minimization of the total free energy (ref. 1) provide a useful tool for determining the equilibrium composition in a gas-solid system. Such calculations have been used to determine the equilibrium partial pressures of gaseous reaction products for the SiC-H₂ system (refs. 2 and 3) and to determine the stability of SiC and Si₃N₄ in environments containing H₂ and small amounts of moisture (ref. 4). The effects of pressure and temperature on the stability of SiC and Si₃N₄ were not considered in these studies.

The objective of this study was to examine, by means of thermochemical analysis, the chemical stability of different ceramic materials in H₂-containing environments as a function of temperature, total system pressure, and moisture content in the atmosphere. These equilibrium calculations are helpful in defining the upper temperature limits for the ceramic materials in H₂-containing environments.

Ceramic Materials Considered

The following ceramic materials were considered in this study: SiC, Si₃N₄, SiO₂, Al₂O₃, mullite, ZrO₂, Y₂O₃, CaO, MgO, BeO, TiB₂, TiC, HfC, and ZrC. Among these ceramic materials, SiC, Si₃N₄, Al₂O₃, mullite, ZrO₂, and BeO are potential monolithic materials or matrix materials for potential composite systems. The ceramic materials TiB₂, ZrB₂, TiC, HfC, and ZrC might have potential as fiber materials in different ceramic-matrix composites. The oxides Y₂O₃, CaO, and MgO were considered because they are used to stabilize ZrO₂. Also, MgO and Y₂O₃ are frequently added as sintering aids to Si₃N₄. The oxide SiO₂ is formed on SiC and Si₃N₄ in oxidizing environments and offers protection against further oxidation.

Method of Calculation and Thermodynamic Data

All of the equilibrium calculations were performed with the computer program SOLGASMIX-PV that was originally developed by Eriksson et al. (ref. 1) and later modified by Besmann (ref. 5). This computer program is based on the principle of minimization of the Gibbs free energy of the system. The thermodynamic data for all relevant species except Si₂ON₂, β -Si₃N₄, Hf(g), Zr(g), Y(g), and YO(g) were obtained from standard sources such as the JANAF Thermochemical Tables (ref. 6) and the compilations by Barin and Knacke (ref. 7). The thermodynamic data for Si₂ON₂ and β -Si₃N₄ were taken from the work of Hendry (ref. 8); the data for Hf(g), Zr(g), and Y(g) were taken from compilations by Hultgren (ref. 9); and that for YO(g) from the work of Ruzinov (ref. 10).

Stability of SiC

Stability in Pure H₂

Thermodynamic calculations show that SiC would decompose to Si in pure hydrogen. The equilibrium partial pressures for the major gaseous product species (i.e., CH₄, SiH₄, and SiH) as a function of temperature are shown in figure 1. There are other gaseous products; however, their equilibrium partial pressures are orders of magnitude lower than those of the species shown in figure 1. The gaseous species CH₄ is the predominant reaction product at all temperatures. The primary mode of reaction between SiC and H₂ can therefore be written as follows:



The effect of total system pressure on the equilibrium partial pressures of SiH, SiH₄, and CH₄ at 1673 K is shown in figure 2. The partial pressures of these gaseous species increase with an increase in total pressure, suggesting that the extent of reaction between SiC and H₂ would increase with increases in total system pressure.

Stability in H₂ + H₂O Mixtures at 1-atm Total Pressure

Figure 3 shows the solid products and the equilibrium partial pressures of major product gases as a function of moisture content for temperatures ranging from 1173 to 1673 K. The results shown at 1673 K are similar to those obtained by Kim (ref. 4). Four distinct stability regimes are evident from this figure and are described here. (Stability regime IV is not shown at 1673 K.)

Regime I.—Regime I corresponds to low moisture contents in the atmosphere. Solid Si and SiC are the stable solids in this regime. The gaseous products CH₄, SiH₄, SiH, CO, and SiO are predominant. The partial pressures of CH₄, SiH, and SiH₄ remain constant, whereas the partial pressures of SiO

and CO increase with increasing moisture content. The relative stability of SiH with respect to SiH₄ decreases with a decrease in temperature, and at temperatures below 1473 K, the partial pressure of SiH is considerably lower than that of SiH₄. Partial pressures of SiH are therefore not shown in the stability diagrams for temperatures at or below 1473 K.

Because Si is the only solid product formed in this regime and because the partial pressure of CH₄ is considerably higher than those of other gaseous species, the primary mode of degradation in this regime is likely to be the reaction of SiC with H₂ to form Si and CH₄ by reaction (1). This process is similar to that which takes place in pure hydrogen.

Regime II.—At higher temperatures (i.e., in the temperature range 1373 to 1673 K), SiC is the only solid that is stable in regime II. The predominant gaseous species in this regime are SiO, CO, and CH₄. The stability of CO relative to that of CH₄ increases either with increasing temperature or with increasing moisture content in the atmosphere. For example, at 1673 K, SiO and CO are the predominant gaseous species for higher moisture levels, whereas SiO and CH₄ are predominant for lower moisture levels. At 1473 K, SiO and CH₄ are the major gaseous products for all moisture levels corresponding to regime II.

Because SiC is the only stable solid phase in this regime, active oxidation of SiC is the primary mode of degradation here. The width of this active oxidation domain decreases with temperature.

At temperatures below 1273 K, the solid species stable in regime II are SiC, Si, and SiO₂. The partial pressures of all major gaseous products remain constant in this regime. The ratio of SiO₂ to Si increases with an increase in the moisture content. The stability domain widens with a decrease in temperature. The solid species Si plus SiO₂ exist in equilibrium with SiC at lower temperatures because SiO(g) becomes less stable with decreasing temperature.

Regime III.—The stable solid species in regime III are SiC and SiO₂. Formation of a SiO₂ layer on SiC is likely to provide protection against further oxidation; therefore this regime may be called the domain of passive oxidation.

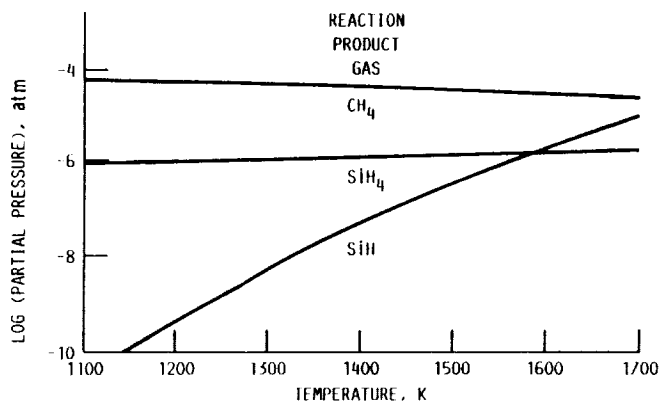


Figure 1.—Equilibrium partial pressures of reaction product gases as a function of temperature for reaction of SiC with pure H₂ at a total pressure of 1 atm.

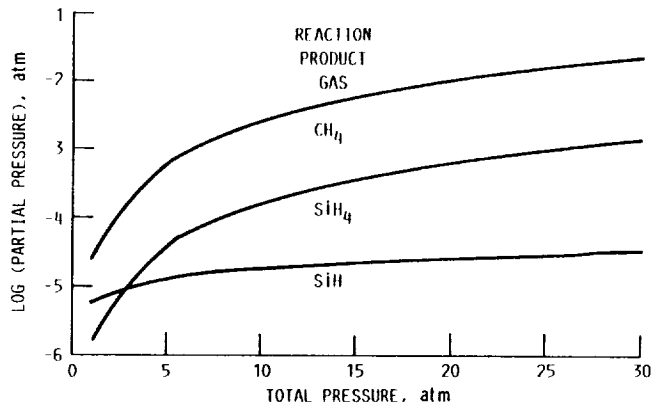
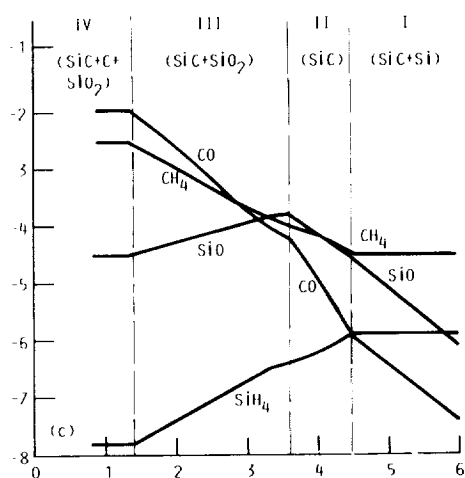
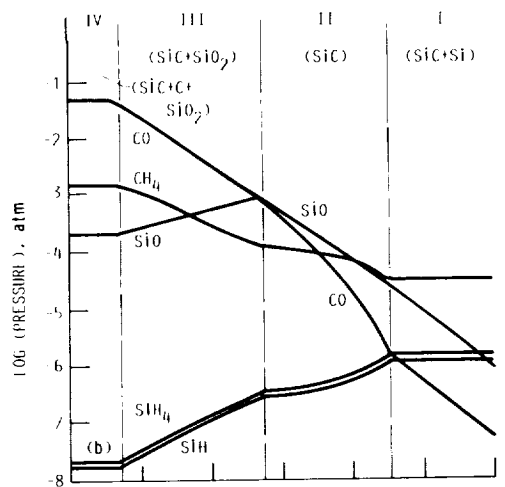
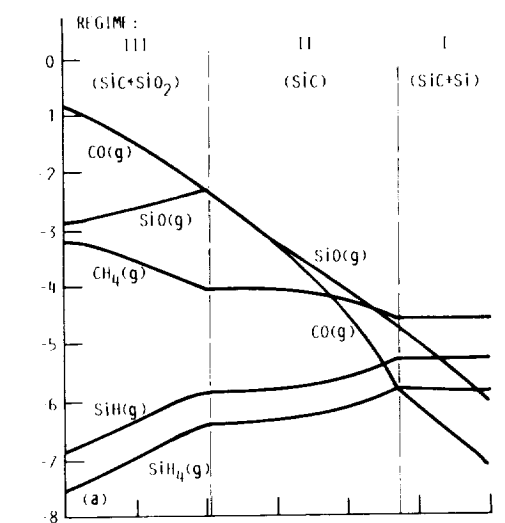
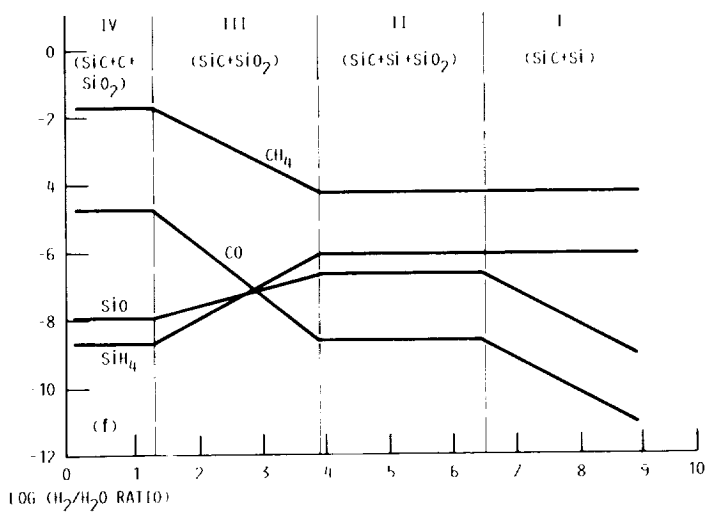
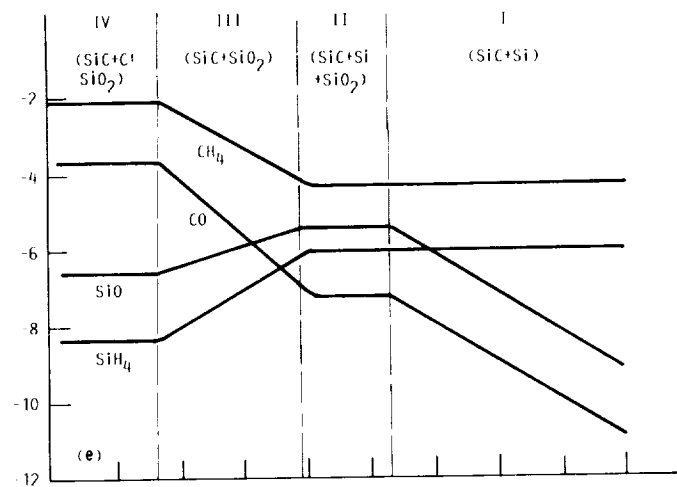
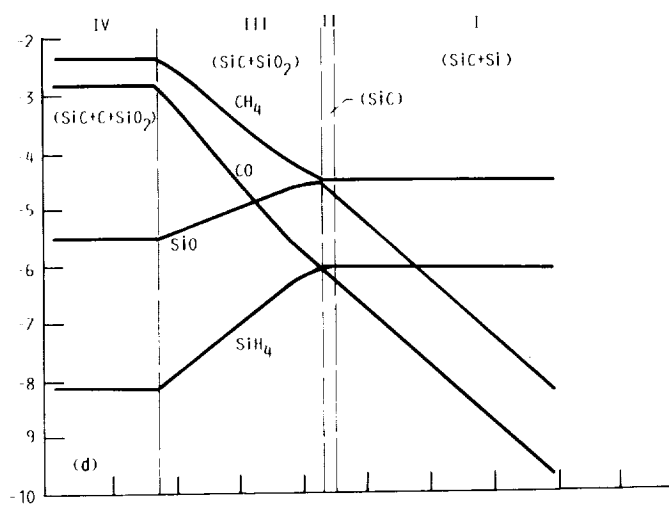


Figure 2.—Effect of total pressure on partial pressures of reaction product gases for reaction of SiC with pure hydrogen at 1673 K.



(a) Temperature, 1673 K.
(b) Temperature, 1573 K.
(c) Temperature, 1473 K.



(d) Temperature, 1373 K.
(e) Temperature, 1273 K.
(f) Temperature, 1173 K.

Figure 3.—Stability of SiC in $H_2 + H_2O$ atmospheres for 1-atm total pressure.

Regime IV.—Regime IV is present at higher moisture levels in the atmosphere. The stable solid species at equilibrium in this regime are SiC, C, and SiO₂.

Effect of Total Pressure on Stability of SiC in H₂ + H₂O Atmospheres

Figure 4 shows the effect of total pressure on the stability of SiC in H₂ + H₂O atmospheres at 1673 K. The general features of the stability regimes are the same as those at 1-atm total pressure. However, the width of regime II, the domain of active oxidation, decreases with increasing total pressure, and the region of active oxidation completely disappears above a certain total pressure (~15 atm). Instead, both Si and SiO₂ are formed at high pressures in equilibrium with SiC in regime II. Increasing the total pressure thus has the same effect as decreasing the temperature at 1-atm total pressure.

Moisture Level Required for SiO₂ Formation on SiC

Because a layer of SiO₂ on a SiC surface is likely to provide protection against further oxidation, it becomes important to know the critical moisture level required for its formation on the SiC surface. This is shown in figure 5. The moisture levels shown in this figure correspond to the transition from regime II to III. Although SiO₂ is formed in stability regime II at lower temperatures, it is formed along with Si and therefore it is doubtful whether a continuous layer of SiO₂ can be developed in this regime.

As shown in figure 5, the moisture level required for SiO₂ formation at 1-atm total pressure decreases with decreasing temperature up to 1373 K and then increases with a further decrease in temperature. Increases in total system pressure have two effects on the moisture-required-for-SiO₂-formation-versus-temperature curve: (1) the inflection in the moisture-versus-temperature curve is shifted toward the right (i.e., toward higher temperatures) with an increase in total system pressure, and (2) the curve is shifted downward (i.e., toward higher moisture levels) with an increase in total system pressure. Thus, the effect of total pressure on the stability of SiC is a function of the temperature. For example, the moisture level required at 1373 K for SiO₂ formation on the SiC surface increases with increasing total system pressure. On the other hand, the moisture level required at 1673 K for SiO₂ formation on the SiC surface decreases with increasing total pressure in the range 1 to 20 atm, and then increases with a further increase in total pressure.

Stability of Si₃N₄

Reaction of Si₃N₄ With Pure Hydrogen

Equilibrium calculations show that the reaction of Si₃N₄ with pure H₂ would lead to the formation of pure Si along with the generation of N₂, NH₃, SiH, and SiH₄ as gaseous

products. Although there are other gaseous products, these four are the major product species.

The partial pressures of N₂, NH₃, SiH, and SiH₄ as a function of temperature are shown in figure 6. At temperatures above ~1500 K, the equilibrium partial pressure of N₂ is an order of magnitude greater than those of SiH₄ and SiH. Therefore, N₂ would be the predominant gaseous product species at these temperatures. On the other hand, at temperatures below 1373 K, both N₂ and SiH₄ are the predominant product species in the gas phase. Also, the partial pressures of NH₃ become significant at lower temperatures.

Large partial pressures of N₂, relative to those of H-containing gaseous species at higher temperatures, suggest that decomposition of Si₃N₄ to Si and N₂ by the reaction



is the primary mode of degradation at higher temperatures. If decomposition of Si₃N₄ is the primary reaction at higher temperatures, H₂ is not expected to play any role at these temperatures. Similar decomposition behavior can also be expected if Si₃N₄ is heated in an inert atmosphere such as Ar. Indeed, as shown in figure 7, the partial pressures of N₂ over Si₃N₄ in an inert atmosphere are exactly the same as those obtained for Si₃N₄ in pure H₂ for temperatures above 1373 K but lower for temperatures below 1373 K. At lower temperatures, the presence of H₂ clearly increases the decomposition of Si₃N₄. As shown in figure 6, the partial pressures of N₂ and SiH₄ are of the same order of magnitude at lower temperatures. Greater decomposition of Si₃N₄ at these temperatures must thus be due to the reaction of Si₃N₄ with H₂, resulting in the formation of SiH₄. (Removal of Si in the form of SiH₄ will release the nitrogen component of Si₃N₄.)

Stability of Si₃N₄ in H₂ + H₂O Atmospheres at 1-atm Total Pressure

The stability regimes at 1673 and 1573 are shown in figure 8(a) and (b). The characteristics of the stability diagrams at these temperatures are similar, and three distinct stability regimes are evident from these diagrams. These three stability regimes are described in detail in the following paragraphs.

Regime I.—Regime I corresponds to low moisture levels, and Si₃N₄ plus Si are the stable solid phases in this regime. Nitrogen is the predominant product gas in this regime. The partial pressure of N₂ is the same as the decomposition N₂ pressure over Si₃N₄, which is the equilibrium partial pressure of N₂ if Si₃N₄ is heated in an inert atmosphere. This suggests that the decomposition of Si₃N₄ to Si and N₂ is the primary mode of reaction in this regime. Hydrogen and moisture in the atmosphere clearly do not have any significant effect on the overall reaction in this regime.

Regime II.—Regime II corresponds to intermediate moisture contents. The stable solid phases in regime II are Si and

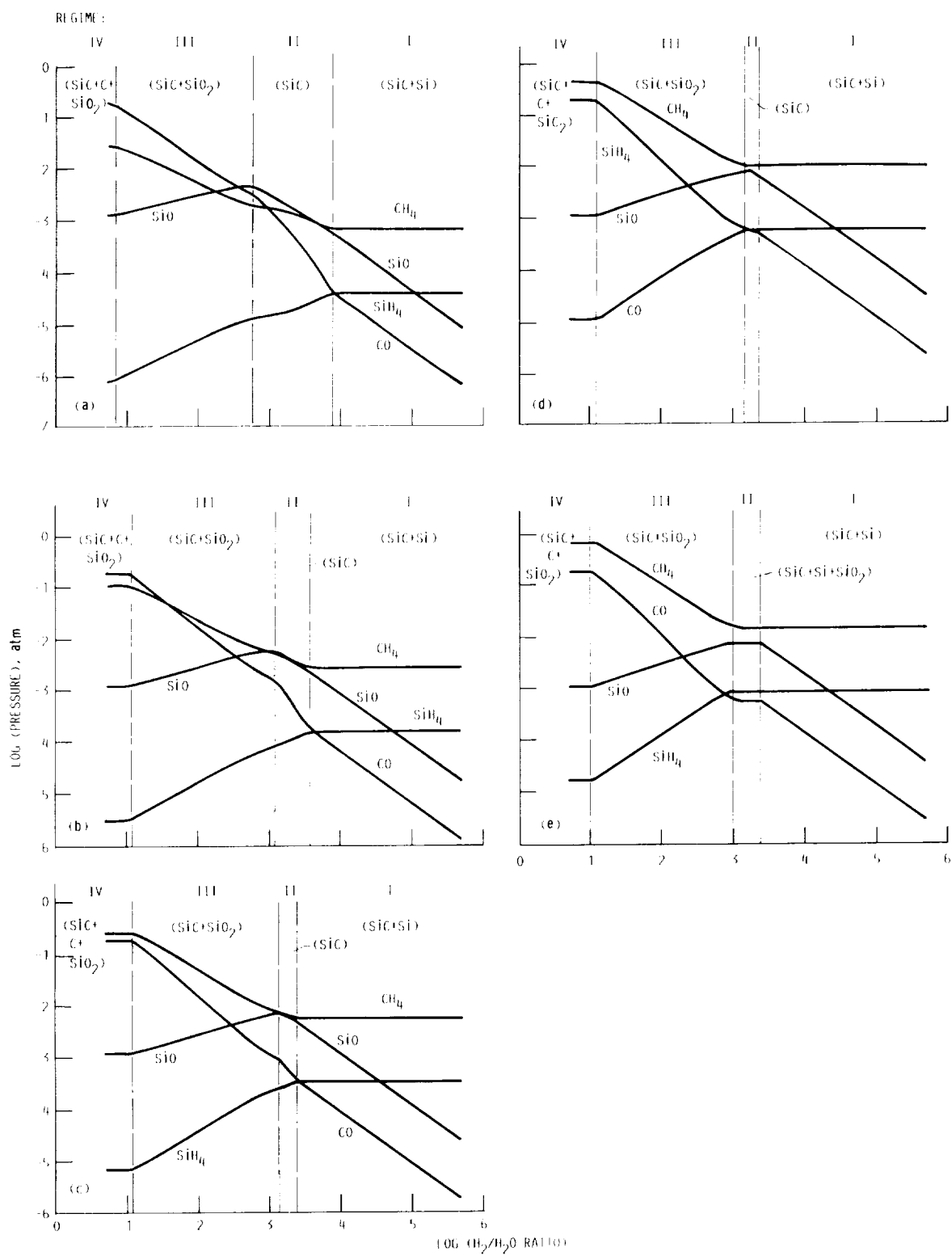


Figure 4.—Stability of SiC in $H_2 + H_2O$ atmospheres at 1673 K as a function of total pressure.

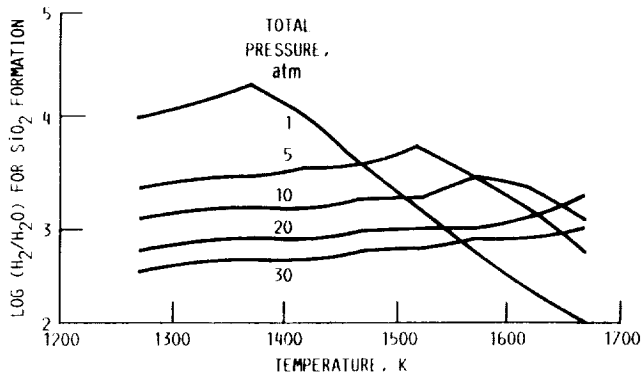


Figure 5.—Moisture level required for SiO_2 formation in $\text{SiC-H}_2\text{-H}_2\text{O}$ system as a function of temperature and total system pressure.

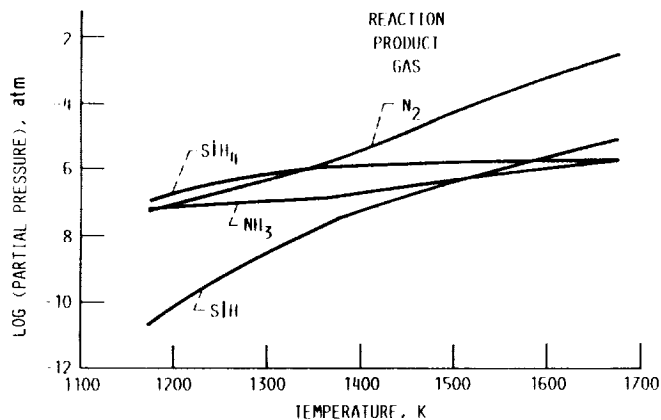


Figure 6.—Equilibrium partial pressures of reaction product gases for reaction of Si_3N_4 with H_2 as a function of temperature for 1-atm total pressure.

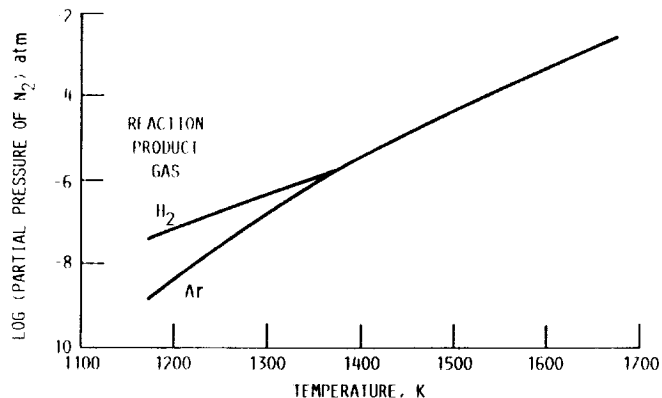


Figure 7.—Comparison of equilibrium partial pressure of $\text{N}_2(\text{g})$ for $\text{Si}_3\text{N}_4\text{-H}_2$ and $\text{Si}_3\text{N}_4\text{-Ar}$ equilibria as a function of temperature for 1-atm total pressure.

Si_2ON_2 along with Si_3N_4 . The partial pressures of N_2 , NH_3 , SiH , SiH_4 , and SiO remain constant in this regime. The amount of Si_2ON_2 in the solid phase increases with increasing moisture content. The partial pressure of N_2 is the same as the decomposition N_2 pressure for Si_3N_4 . This suggests that the decomposition of Si_3N_4 to Si and N_2 is also the primary mode of reaction in this regime.

Regime III.—Regime III corresponds to higher moisture contents. The equilibrium solid phases in this regime are Si_2ON_2 and Si_3N_4 . Although Si_2ON_2 is the solid product that is in equilibrium with Si_3N_4 , an examination of the stability of Si_2ON_2 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres (fig. 9) shows that Si_2ON_2 would convert to SiO_2 at moisture contents corresponding to this regime. The oxide scale on Si_3N_4 in regime III would thus consist of an outer layer of SiO_2 and an inner layer of Si_2ON_2 next to the Si_3N_4 surface.

The stability diagrams at 1473 and 1373 K, shown in figure 8(c) and (d), also indicate three distinct regimes. The general features for stability regimes I and III are similar to those at 1673 and 1573 K, whereas stability regime II is distinctly different from that at higher temperatures. Note that Si_3N_4 is the only solid that is stable in regime II at 1473 K. This is in contrast to the behavior at 1673 and 1573 K, where both Si and Si_2ON_2 are in equilibrium with Si_3N_4 in stability regime II. The gaseous species SiO and N_2 are the predominant ones in regime II at 1473 and 1373 K. Because Si_3N_4 is the only solid that is stable in regime II at 1473 K, active oxidation of Si_3N_4 , resulting in the formation of $\text{SiO}(\text{g})$ and $\text{N}_2(\text{g})$, would be the primary degradation mode in this regime. Stability regime II (i.e., the domain of active oxidation) widens with decreases in temperature.

Only two stability regimes are evident in the stability diagram at 1273 K (fig. 8(e)). In stability regime I, which corresponds to very low moisture levels, Si_3N_4 is the only stable solid. Active oxidation of Si_3N_4 would thus be the predominant degradation mode in this regime. Note that the features corresponding to regime I at higher temperatures (i.e., decomposition of Si_3N_4 to Si and N_2) are completely absent at this temperature. Although figure 8(e) shows stability regimes for moisture contents greater than 0.1 ppm, calculations for much lower moisture contents, such as 0.00001 ppm, did not show any regime where Si is formed. In regime II, SiO_2 is the stable oxide on Si_3N_4 . Again, this is in contrast to the features at higher temperatures where Si_2ON_2 is the stable oxide in contact with Si_3N_4 .

Effect of Total Pressure on Stability of Si_3N_4 in $\text{H}_2 + \text{H}_2\text{O}$ Atmospheres

Figures 10 to 12 show the effect of total system pressure on the stability of Si_3N_4 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at three temperatures: 1673, 1573, and 1473 K. Although the general features of the stability diagram at 1673 K do not change with total system pressure, the phase boundaries are shifted toward the right (i.e., toward lower moisture contents).

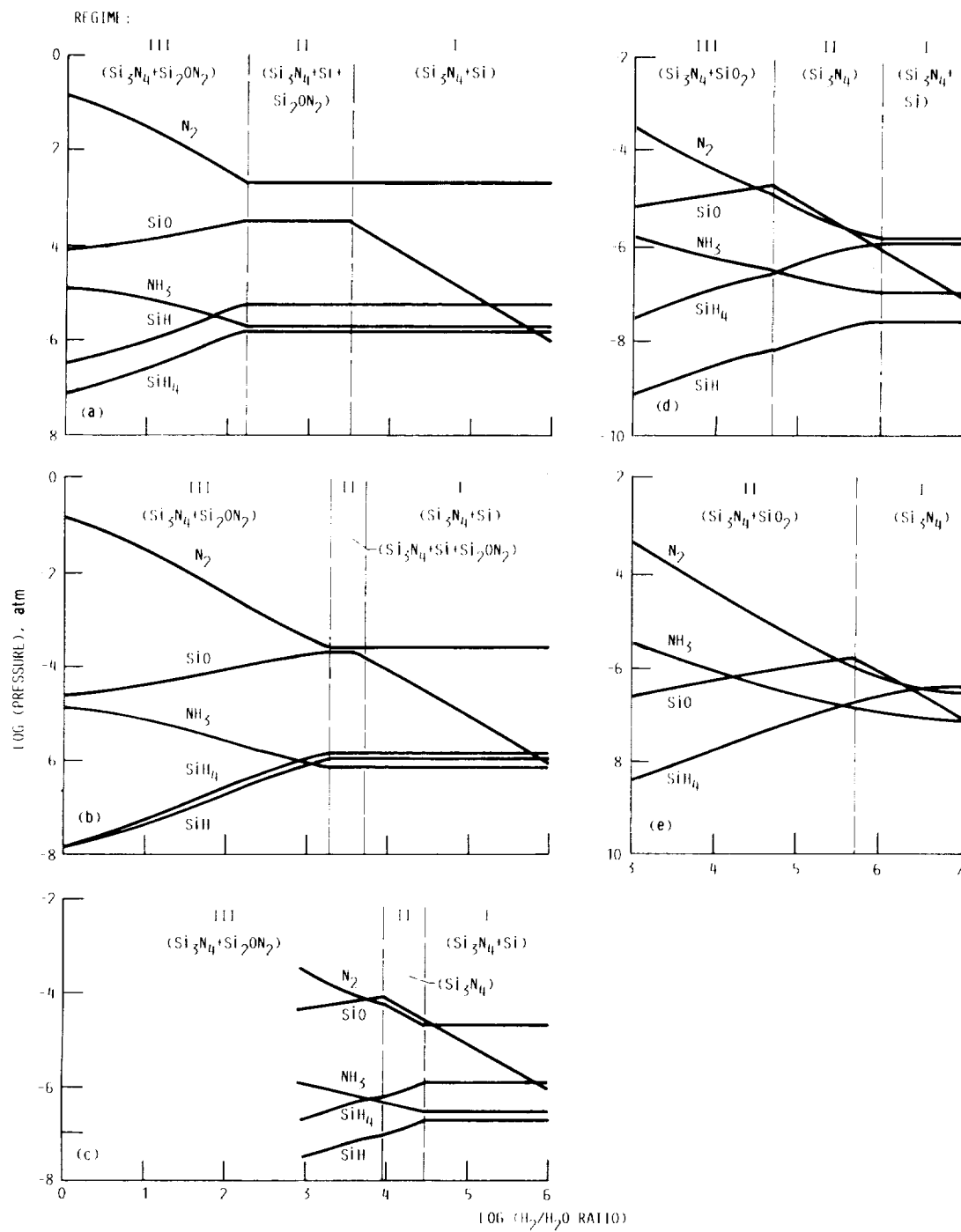


Figure 8.—Stability of Si₃N₄ in H₂ + H₂O atmospheres for 1-atm total pressure.

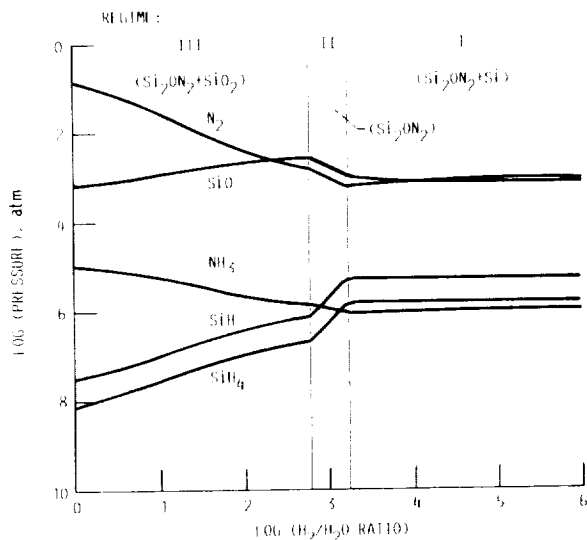
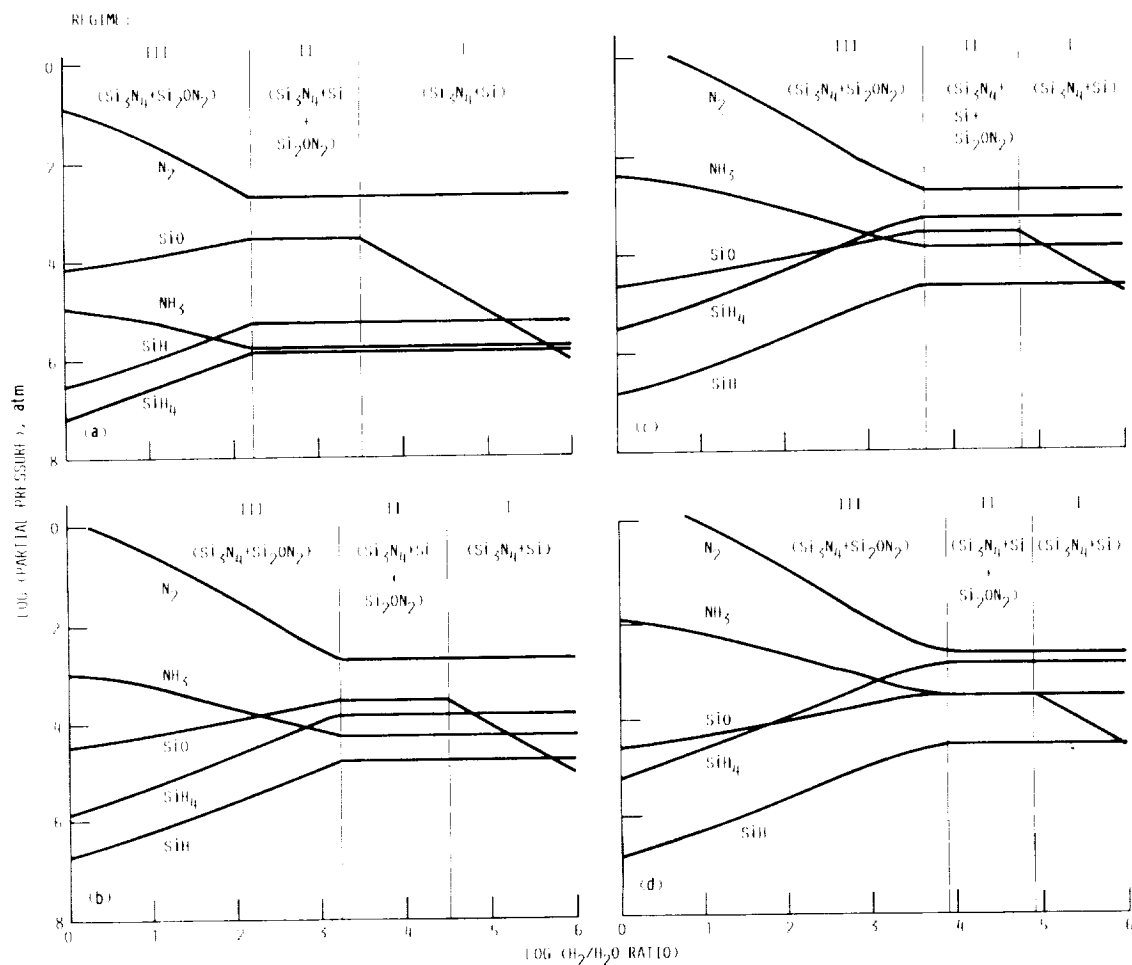


Figure 9.—Stability of Si_2ON_2 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres for 1-atm total pressure.

The effect of total system pressure on the stability of Si_3N_4 is rather more dramatic at lower temperatures. For example, consider the effect of total pressure on the stability of Si_3N_4 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at 1573 K (fig. 11). The general features of the stability diagram are similar for 1- and 10-atm total pressures, and the three stability regimes for both these pressures are $\text{Si}_3\text{N}_4 + \text{Si}$ for low moisture contents, $\text{Si}_3\text{N}_4 + \text{Si} + \text{Si}_2\text{ON}_2$ for intermediate moisture contents, and $\text{Si}_3\text{N}_4 + \text{Si}_2\text{ON}_2$ for high moisture contents. Note that stability regime II is considerably narrower at 10-atm total pressure than at 1-atm total pressure. As the total pressure is increased to 15 atm, three phases (Si , Si_2ON_2 , and Si_3N_4) are no longer present in regime II. Instead, Si_3N_4 is the only stable phase in this regime. The stable solid phases in regimes I and III are similar to those for lower total pressures. As the total pressure is increased to 30 atm, only two regimes are evident in the stability diagram. The only stable solid phase for lower moisture contents is Si_3N_4 ; and the stable solid phases at high moisture contents are Si_3N_4 and Si_2ON_2 . The



(a) Pressure, 1 atm.
(b) Pressure, 10 atm.

(c) Pressure, 20 atm.
(d) Pressure, 30 atm.

Figure 10.—Effect of total pressure on stability of Si_3N_4 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at 1673 K.

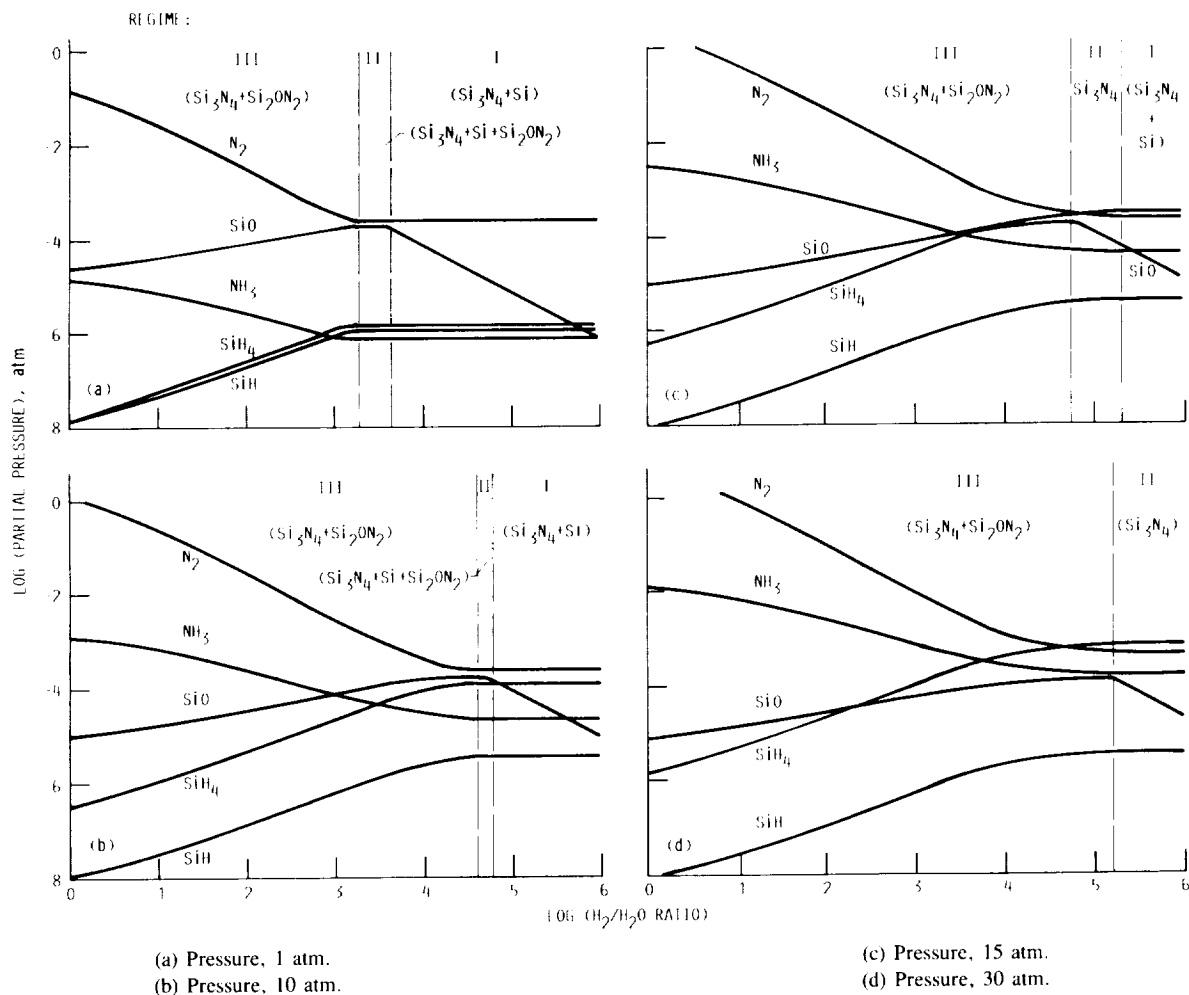


Figure 11.—Effect of total pressure on stability of Si_3N_4 in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at 1573 K.

stability regime in which Si and Si_3N_4 are the stable phases is completely absent at 30-atm total pressure.

At 1473 K (fig. 12), there are two stability regimes for 10-atm total pressure. The stable solid phase for lower moisture contents is Si_3N_4 , and the stable solid phases for higher moisture levels are Si_3N_4 and Si_2ON_2 . The regime corresponding to lower moisture contents for 1-atm total pressure (i.e., the regime in which Si_3N_4 and Si are the two stable solid phases) is no longer present at 10 atm.

Increasing the total system pressure clearly has the same effect as decreasing the temperature at 1-atm total pressure. The stability domain corresponding to active oxidation of Si_3N_4 (i.e., the regime in which Si_3N_4 is the only solid phase) is present only at lower temperatures for 1-atm total pressure. However, active oxidation of Si_3N_4 is possible at higher temperatures if the total system pressure is increased. The predominant gaseous species in the regime corresponding to active oxidation of Si_3N_4 for higher total system pressures are N_2 , SiH_4 , and SiO, and the relative stability of SiH_4 with respect to SiO increases with increasing total pressure. This

is in contrast to the situation for 1-atm total pressure in which the predominant gaseous species in the regime corresponding to the active oxidation of Si_3N_4 are SiO and N_2 . The stability of SiH_4 thus increases with an increase in total system pressure.

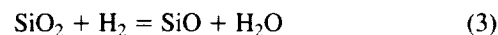
Moisture Level Required for SiO_2 Formation on Si_3N_4

Figure 13 shows the moisture level required for SiO_2 formation as a function of temperature and total system pressure. The amount of moisture in the hydrogen atmosphere required for SiO_2 formation increases with increasing temperature and decreases with increasing total system pressure. About 5000 ppm moisture (0.5 percent) is required for SiO_2 formation at 1673 K and for a total pressure of 1 atm, whereas only 2 ppm moisture is sufficient for SiO_2 formation at 1273 K. In a practical sense, because the so-called "dry hydrogen" always contains a few parts per million of moisture, SiO_2 can be formed on Si_3N_4 at low temperatures (1273 and 1173 K) even in dry hydrogen.

Stability of SiO₂

Stability in Pure Hydrogen

Equilibrium calculations show that SiO is the primary product gas from SiO₂ at high temperatures, whereas SiH₄ is the primary product gas at lower temperatures. The equilibrium partial pressures of SiO and SiH₄ as a function of temperature for 1-atm total pressure are shown in figure 14. For temperatures above ~1273 K, SiO₂ will be reduced by H₂, resulting in the formation of SiO(g) by the reaction



Although the formation of SiH₄ is favored at lower temperatures (i.e., at temperatures lower than 1100 K), the equilibrium partial pressure of SiH₄ at these temperatures is quite low ($< 10^{-7}$ atm), and SiO₂ is therefore likely to be relatively stable in pure H₂ at these temperatures.

The equilibrium partial pressures for SiO and SiH₄ for the SiO₂-H₂ system as a function of total system pressure are shown in figure 15. The relative stability of SiH₄ increases with increasing total system pressure. At 1673 and 1573 K, SiO is still the predominant gaseous species at higher total system pressures. However, for temperatures below 1373 K, SiH₄ becomes the predominant gaseous species at higher total system pressures.

Stability in H₂ + H₂O at 1-atm Total Pressure

Calculations show that SiO(g) is the predominant gaseous species in H₂ + H₂O atmospheres at higher temperatures (temperatures greater than 1200 K). The magnitude of the equilibrium partial pressure of SiO for a given temperature and moisture content would thus determine the relative stability of SiO₂ in H₂ + H₂O atmospheres. For the equilibrium calculations made with the SOLGASMIX program, the initial

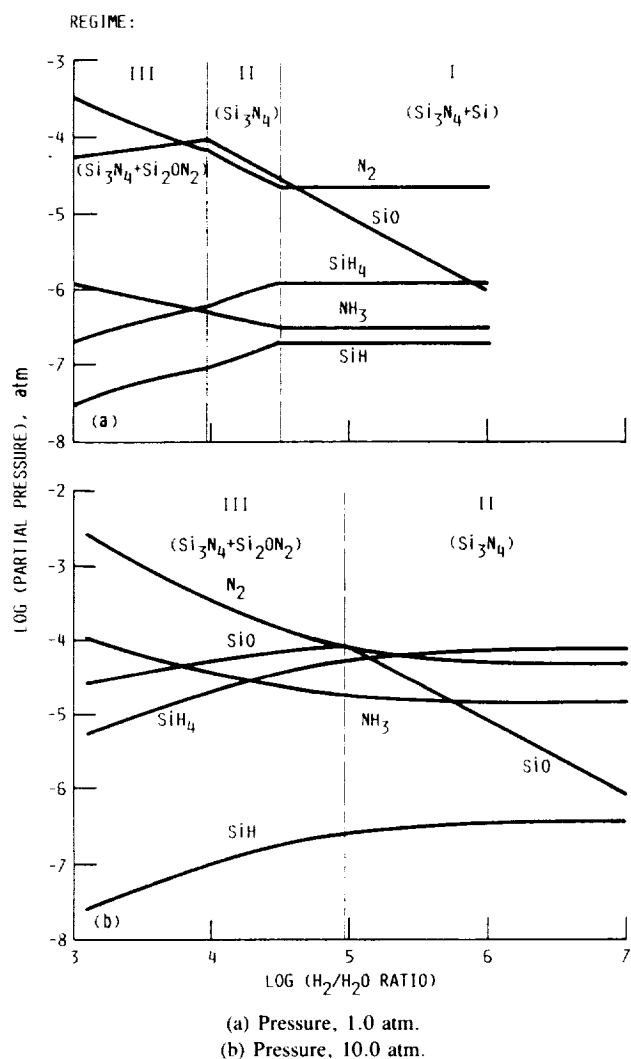


Figure 12.—Effect of total pressure on stability of Si₃N₄ in H₂ + H₂O atmospheres at 1473 K.

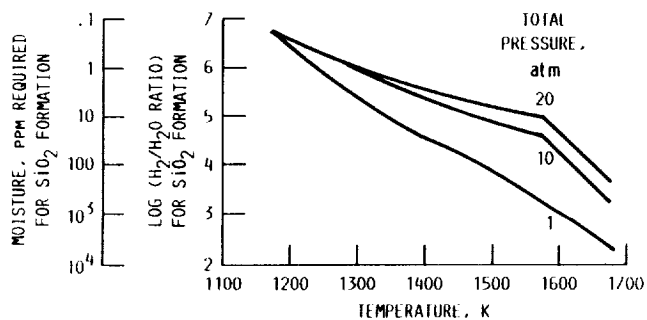


Figure 13.—Effect of total pressure on moisture levels required for SiO₂/Si₂ON₂ formation on Si₃N₄ in H₂ + H₂O atmospheres.

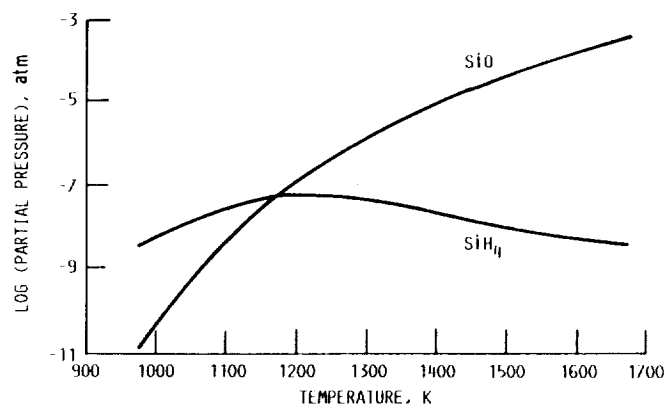
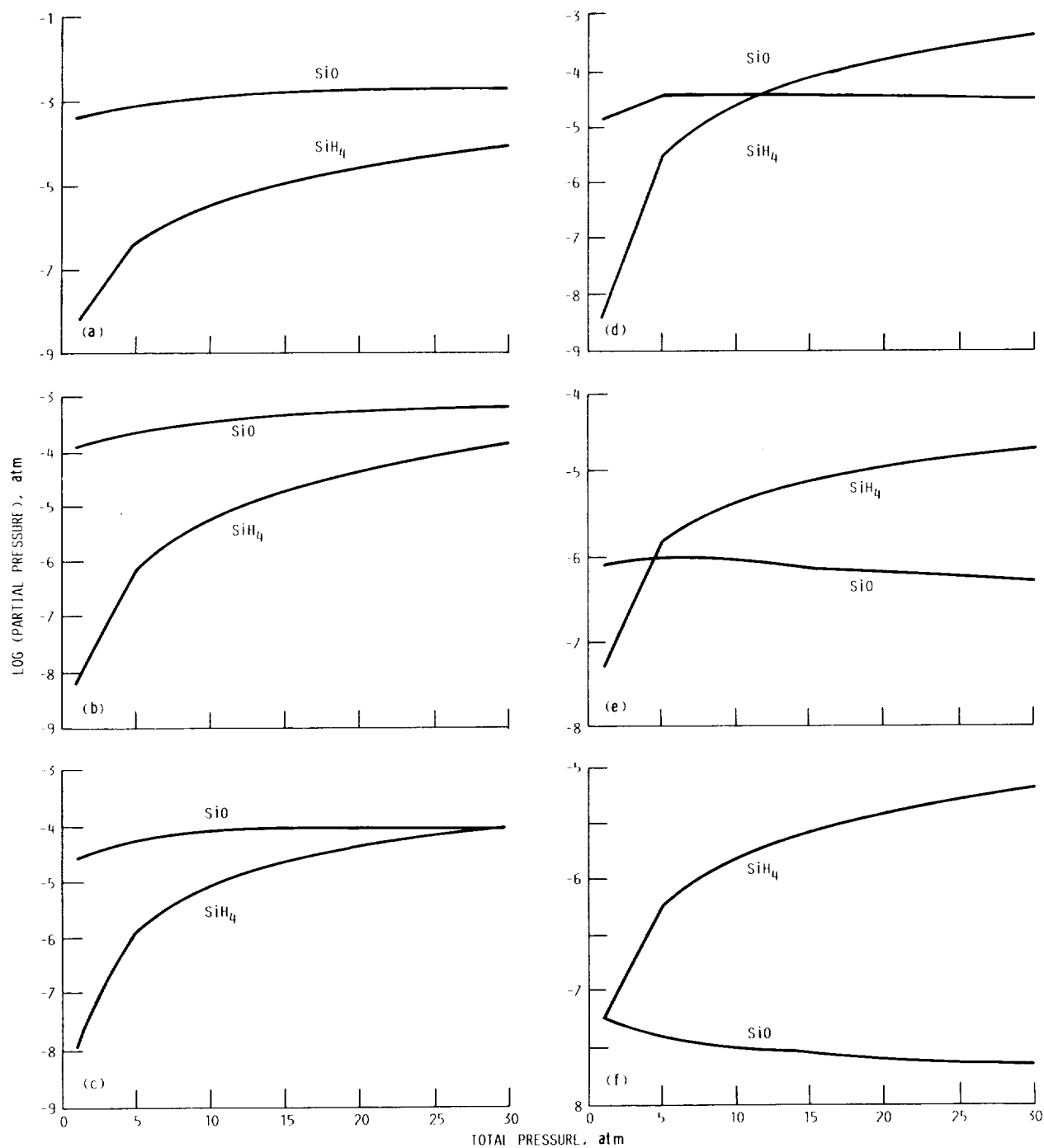


Figure 14.—Partial pressures of reaction product gases (SiO and SiH₄) as a function of temperature for reaction of SiO₂ with pure H₂ at 1-atm total pressure.



(a) Temperature, 1673 K. (d) Temperature, 1373 K.
 (b) Temperature, 1573 K. (e) Temperature, 1273 K.
 (c) Temperature, 1473 K. (f) Temperature, 1173 K.

Figure 15.—Effect of total pressure on the partial pressures of reaction product gases (SiO and SiH₄) for reaction of SiO₂ with pure hydrogen atmosphere.

amounts of all the reactants are fixed, and the equilibrium partial pressures of SiO(g) calculated with this computer program will therefore be somewhat different from those for an open system in which there is continuous replenishment of the reactant gases, H₂ and H₂O. Because it has already been determined that SiO(g) is the predominant gaseous species for the reaction of SiO₂ in H₂ + H₂O atmospheres, the equilibrium partial pressure of SiO in an open system can be calculated from the equilibria for reaction (3).

From the equilibria for reaction (3), the equilibrium partial pressure of SiO can be expressed as

$$\log(p_{\text{SiO}})_{\text{eq}} = \log(K_3) + \log\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) \quad (4)$$

where $(p_{\text{SiO}})_{\text{eq}}$ is the equilibrium partial pressure of SiO(g); p_{H_2} and $p_{\text{H}_2\text{O}}$ are the partial pressures of H₂ and moisture, respectively; and K_3 is the equilibrium constant for reaction (3).

Figure 16 shows the equilibrium partial pressure of SiO(g) as a function of moisture content in the atmosphere for five temperatures. The equilibrium partial pressure of SiO decreases with increasing moisture content and increases with increasing temperature. Figure 16 can offer some guidelines regarding the protectiveness of a SiO₂ scale formed on SiC and Si₃N₄ in H₂ + H₂O atmospheres. For example, although SiO₂ can be formed on both SiC and Si₃N₄ at 1673 K at moisture levels greater than about 1 percent, the equilibrium partial pressure of SiO(g) over the SiO₂ surface is on the order of 10⁻⁵ atm, which is quite high. Thus, even though a SiO₂ layer would be formed at 1 percent H₂O, the rate of oxidation in such an atmosphere would be higher because of the formation of SiO(g).

Effect of Total Pressure in H₂ + H₂O

Figures 17 and 18 show the effect of total pressure on the equilibrium partial pressures of SiO and SiH₄ for the reaction of SiO₂ with H₂ at two moisture levels, 10 and 100 ppm. The total system pressure does not have any significant effect on the equilibrium partial pressure of SiO. On the other hand, the equilibrium partial pressure of SiH₄ increases with increasing total pressure. For higher moisture levels in the atmosphere (>100 ppm or so), SiO would still be the predominant gaseous product species at higher total pressures for temperatures in the range 1273 to 1673 K. However, for lower moisture levels (10 ppm or so), SiH₄ would be important at lower temperatures for higher system pressures.

Stability of Al₂O₃

Stability in Pure H₂

Equilibrium calculations show that Al₂O₃ is the only condensed phase in equilibrium with H₂; no liquid Al is

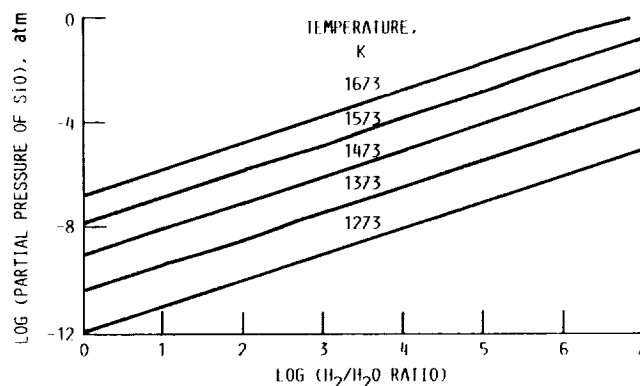


Figure 16.—Equilibrium partial pressure of SiO(g) for the reaction SiO₂ + H₂ = SiO + H₂O as a function of temperature and H₂/H₂O ratio.

formed as a result of the reaction of Al₂O₃ with pure H₂. The gaseous species Al(g) and Al₂O(g) are the predominant reaction products. Figure 19 shows the equilibrium partial pressures of Al(g) and Al₂O(g) for Al₂O₃-H₂ equilibria as a function of temperature for 1-atm total pressure. The equilibrium partial pressures for Al₂O(g) are an order of magnitude lower than that of Al(g). Thus, Al(g) is expected to be the primary reaction product for the Al₂O₃-H₂ system.

Stability in H₂ + H₂O Atmospheres

Figure 20 shows the equilibrium partial pressures of various product gases for the reaction of Al₂O₃ in H₂ + H₂O atmospheres at 1673 and 1873 K for 1-atm total pressure. Alumina is the only stable condensed species and Al(g) is the predominant gaseous reaction product. For low moisture contents (2 to 3 ppm at 1673 K and up to about 10 ppm at 1873 K), the equilibrium partial pressure of Al(g) is the same as that for reaction with pure H₂. For moisture contents greater than 10 ppm, the equilibrium partial pressure of Al(g) decreases with increasing moisture content and is extremely low at high moisture levels. For a given moisture level, the equilibrium partial pressure of Al(g) increases with increasing temperature, as shown in figure 21.

Effect of Total System Pressure

The equilibrium partial pressures of Al(g) and Al₂O(g) as a function of total system pressure at 1873 K are shown in figure 22 for three moisture levels: 0 (pure H₂), 100, and 1000 ppm. For pure H₂, the partial pressures of both the gases increase slightly with increasing total system pressure. On the other hand, total system pressure has no effect on the partial pressures of these two gases in moisture-containing atmospheres. The system pressure thus has negligible effect on the stability of Al₂O₃ in H₂ + H₂O environments.

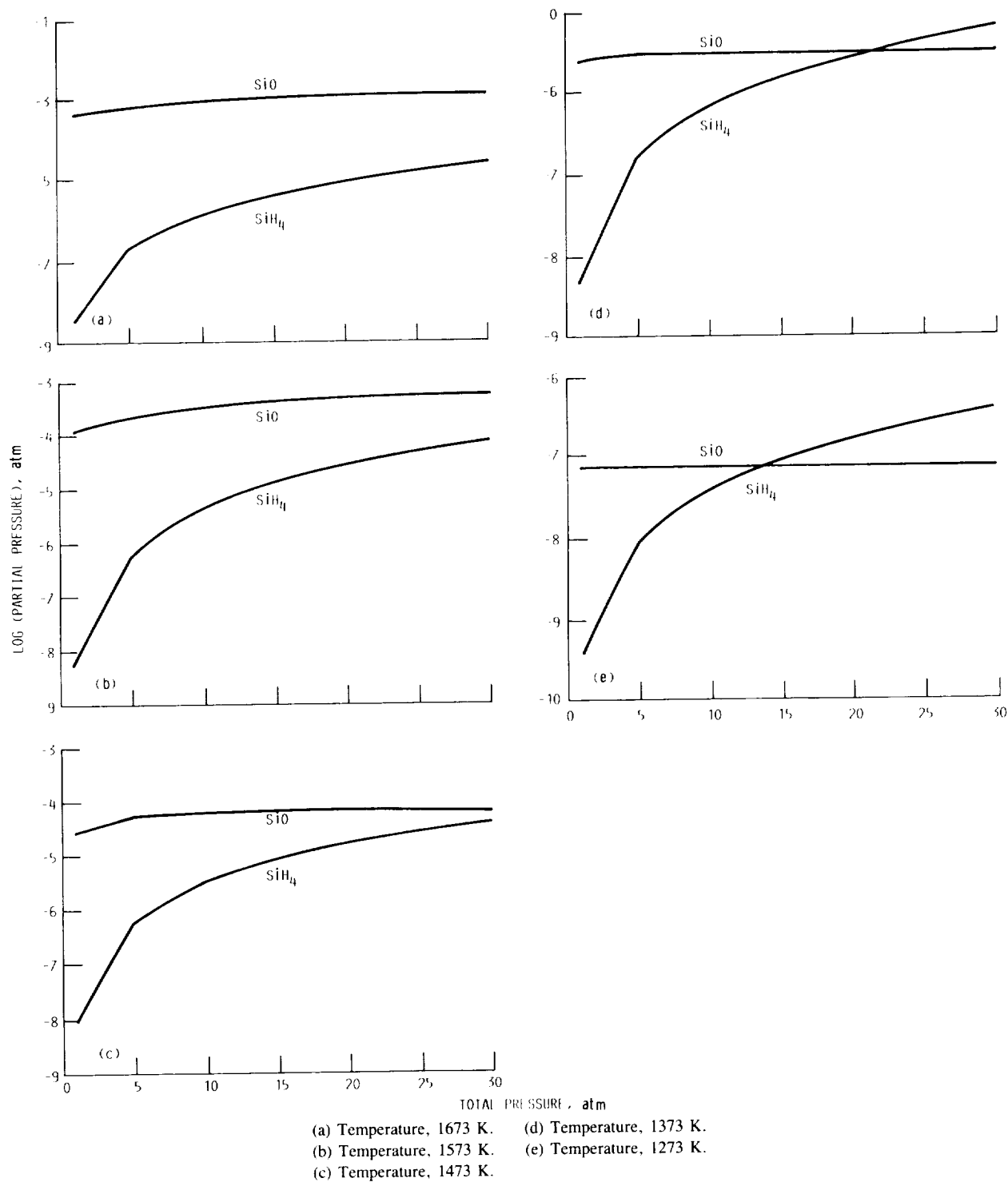


Figure 17.—Effect of total pressure on the partial pressures of SiO(g) and SiH₄(g) for reaction of SiO₂ with H₂ + 10 ppm H₂O.

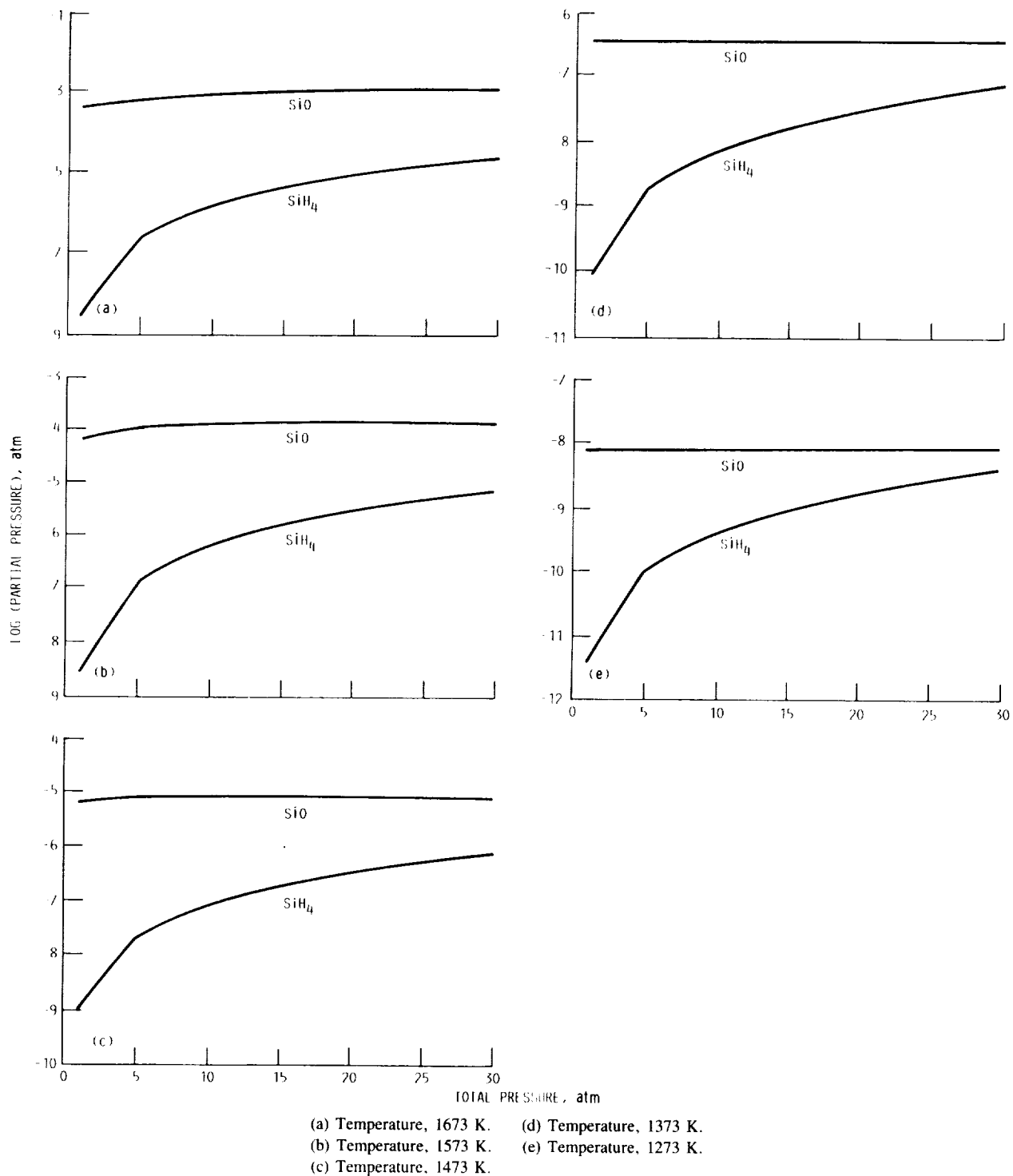


Figure 18.—Effect of total pressure on the partial pressures of SiO and SiH_4 for reaction of SiO_2 with H_2 + 100 ppm H_2O .

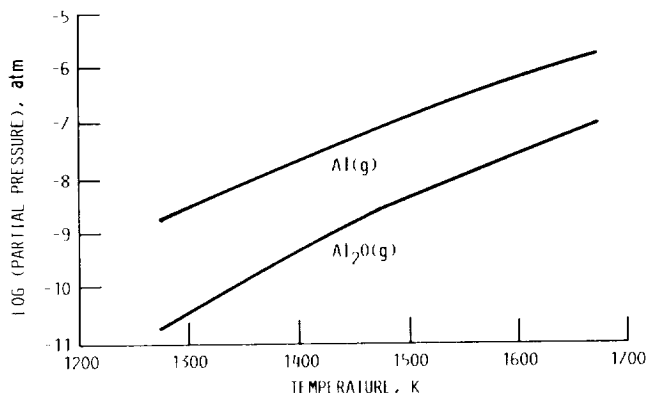
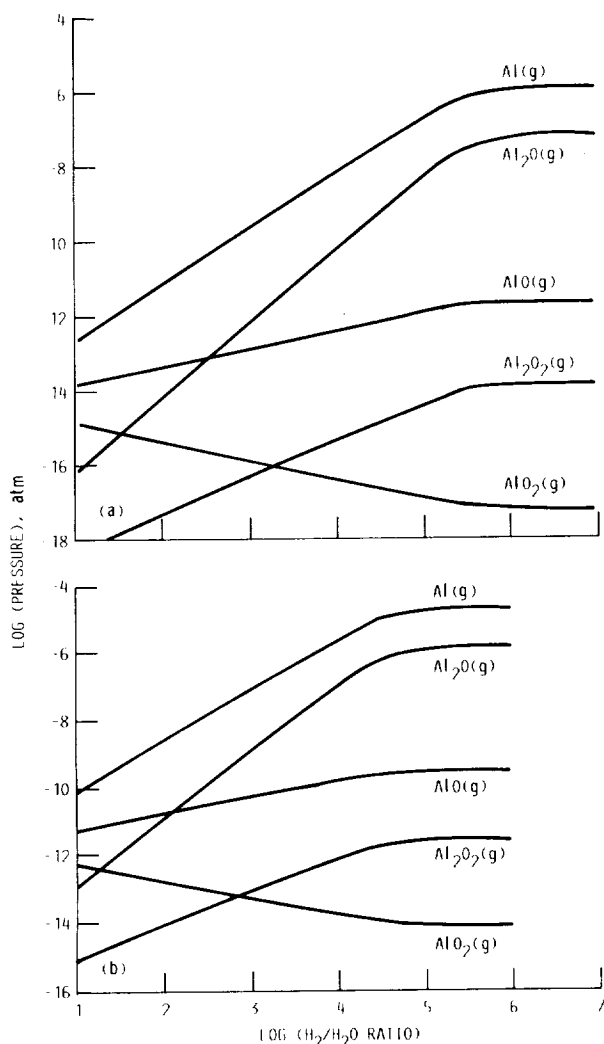


Figure 19.—Equilibrium partial pressures of Al(g) and Al₂O(g) for Al₂O₃-H₂ equilibria at 1-atm total pressure.



(a) Temperature, 1673 K.
(b) Temperature, 1873 K.

Figure 20.—Partial pressures of various reaction product gases as a function of moisture content for reaction of Al₂O₃ with H₂/H₂O environments for a total pressure of 1 atm.

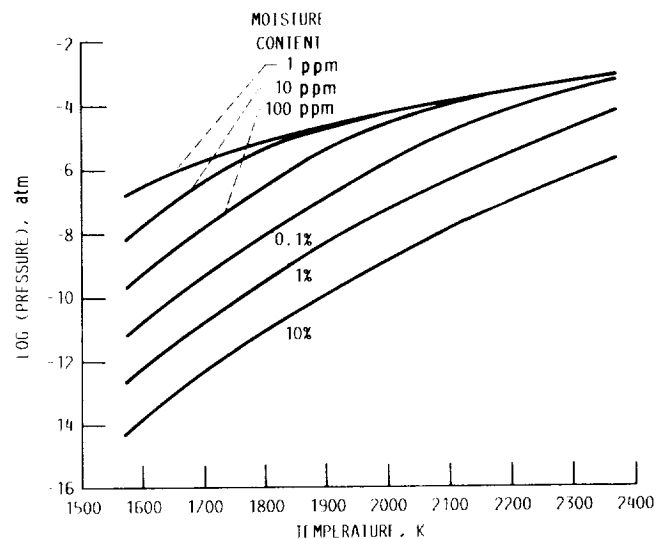


Figure 21.—Partial pressure of Al(g) as a function of temperature and moisture content for reaction of Al₂O₃ with H₂ + H₂O atmospheres for a total pressure of 1 atm.

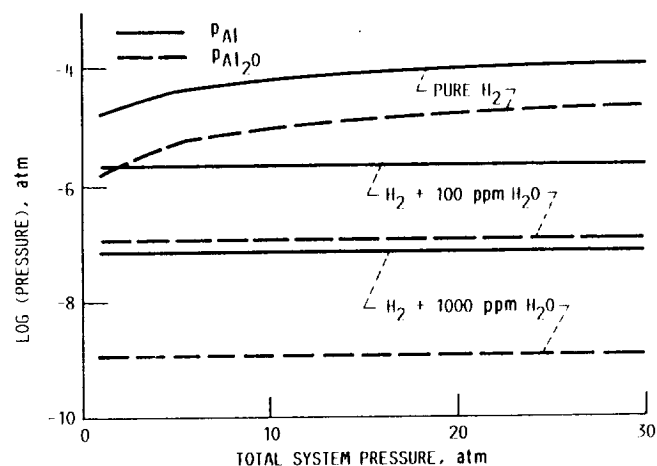


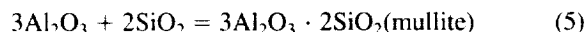
Figure 22.—Equilibrium partial pressures of Al(g) and Al₂O(g) as a function of total system pressure for reaction of Al₂O₃ with H₂/H₂O environments at 1873 K.

Stability of Mullite

The chemical stability of mullite (3Al₂O₃ · 2SiO₂) in hydrogen-containing environments would depend upon the stability of its constituent oxides, Al₂O₃ and SiO₂. Because the equilibrium partial pressures of the gaseous products for the reaction of Al₂O₃ in H₂ + H₂O atmospheres are considerably lower than those for the reaction of SiO₂ in the same atmosphere, the reaction of the SiO₂ constituent of mullite would be of major concern in determining its stability in H₂ + H₂O environments.

The reaction of the SiO₂ constituent of mullite with H₂ + H₂O atmospheres would be a function of the activity of SiO₂. The activity of SiO₂ in mullite in equilibrium with SiO₂

is unity, and the stability of mullite in equilibrium with SiO_2 would therefore be the same as that for pure SiO_2 . The activity of SiO_2 in mullite that is in equilibrium with Al_2O_3 can be determined from the equilibria for the reaction



The activity of mullite is unity and the activity of Al_2O_3 would also be unity for mullite in equilibrium with Al_2O_3 . The equilibrium constant for reaction (5) can thus be written as follows:

$$k_5 = \frac{1}{(a_{\text{SiO}_2})^2} \quad (6)$$

The calculated values for SiO_2 activities for mullite- Al_2O_3 equilibria are given in table I. The equilibrium partial pressures of $\text{SiO}(\text{g})$ for the reaction of SiO_2 at reduced activities with $\text{H}_2 + \text{H}_2\text{O}$ atmospheres can be calculated from the equilibria for reaction (3), that is, from the expression

$$\log(p_{\text{SiO}}) = \log(K_3) + \log\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) + \log(a_{\text{SiO}_2}) \quad (7)$$

The calculated values for equilibrium SiO partial pressures as a function of moisture content and temperature are shown in figure 23 for 1-atm total pressure. The effect of the total system pressure on the stability of mullite in $\text{H}_2 + \text{H}_2\text{O}$ environments would be similar to that for SiO_2 .

TABLE I.—ACTIVITY OF SiO_2 FOR MULLITE- Al_2O_3 EQUILIBRIA

Temperature, K	Activity of SiO_2
1273	0.45
1373	.41
1473	.38
1573	.36
1673	.34

Stability of ZrO_2

Calculations show that ZrO_2 and $\text{Zr}(\text{s})$ would be the stable solid phases in a pure H_2 atmosphere. The major gaseous product species for the reaction of ZrO_2 with pure H_2 are ZrO , ZrH , and $\text{Zr}(\text{g})$. The equilibrium partial pressures of these species as a function of temperature for the ZrO_2 - H_2 equilibria are shown in figure 24. The equilibrium partial pressure of ZrO is orders of magnitude higher than that of the other two gaseous species. Therefore, $\text{ZrO}(\text{g})$ would be

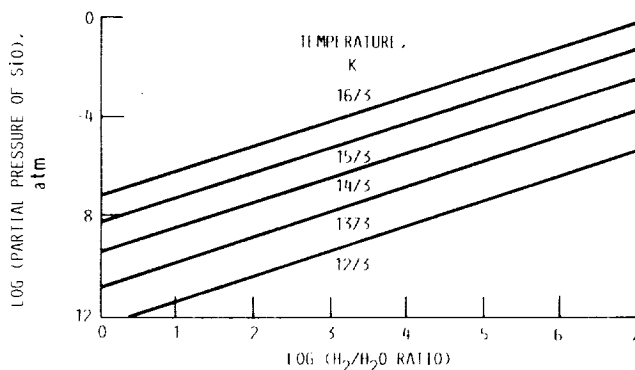


Figure 23.—Partial pressure of $\text{SiO}(\text{g})$ as a function of moisture content and temperature for reaction of mullite with $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at a total pressure of 1 atm.

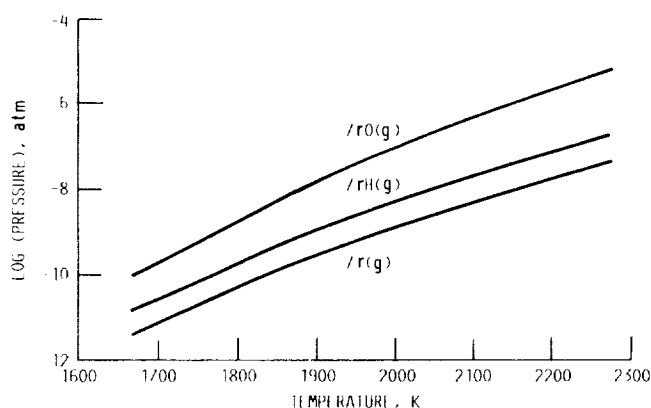


Figure 24.—Equilibrium partial pressure of $\text{ZrO}(\text{g})$, $\text{ZrH}(\text{g})$, and $\text{Zr}(\text{g})$ as a function of temperature for reaction of ZrO_2 with H_2 at a total pressure of 1 atm.

the predominant gaseous product for the reaction of ZrO_2 with pure H_2 .

The equilibrium partial pressures at 1873 K of the major gaseous product species for the reaction of ZrO_2 with moisture-containing environments are shown in figure 25. The compound ZrO_2 is the only stable solid phase in moisture-containing atmospheres. Among the gaseous products, $\text{ZrO}(\text{g})$ is predominant for all moisture levels. Figure 26 shows the partial pressure of $\text{ZrO}(\text{g})$ as a function of temperature and moisture content for the reaction of ZrO_2 with $\text{H}_2 + \text{H}_2\text{O}$ environments at 1-atm total pressure. The partial pressure of ZrO decreases with an increasing moisture content and increases with increasing temperature.

The total system pressure has no significant effect on the stability of ZrO_2 in $\text{H}_2 + \text{H}_2\text{O}$ environments.

Stability of Y_2O_3

The major gaseous products for the reaction of Y_2O_3 in H_2 -containing atmospheres are $\text{Y}(\text{g})$ and $\text{YO}(\text{g})$. The equilibrium partial pressures for these two species as a function

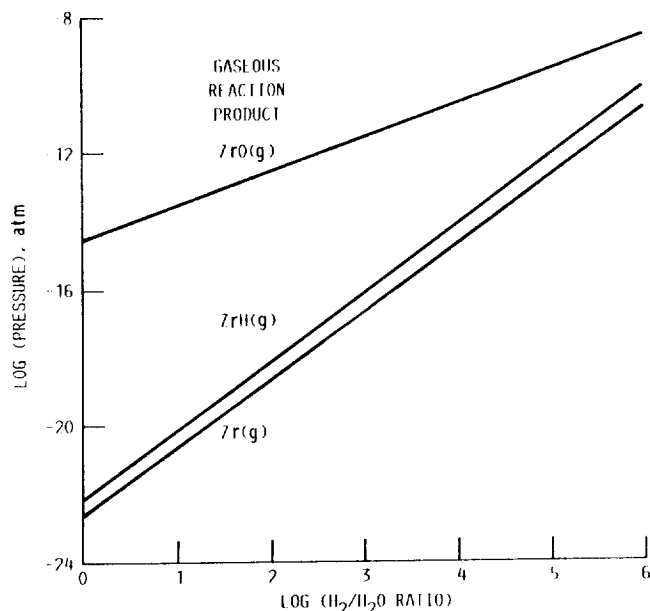


Figure 25.—Partial pressures of gaseous reaction products for reaction of ZrO_2 with $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at 1873 K for a total pressure of 1 atm.

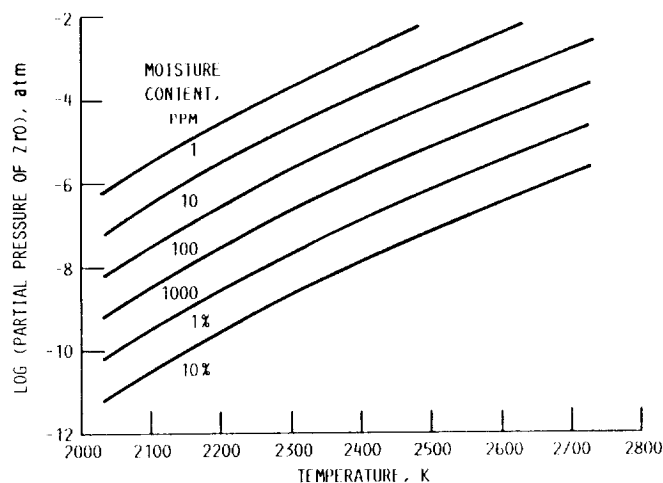


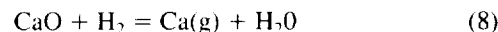
Figure 26.—Equilibrium partial pressure of ZrO(g) as a function of temperature and moisture content for reaction ZrO_2 with $\text{H}_2/\text{H}_2\text{O}$ environments.

of temperature and moisture content are shown in figure 27. The compound Y_2O_3 is the only stable solid phase in both pure H_2 and H_2 atmospheres containing moisture. In pure H_2 , Y(g) is the predominant gaseous product species for temperatures lower than 2173 K, whereas both Y(g) and YO(g) become important at higher temperatures. For low moisture levels (e.g., 10 ppm), YO(g) is the predominant gaseous species at temperatures lower than ~ 2073 K; at temperatures higher than this, both Y(g) and YO(g) are important. At higher moisture levels (e.g., > 100 ppm), YO(g) is the predominant gaseous product species at all temperatures, its partial pressure being a few orders of magnitude greater than that of Y(g) .

The total system pressure has no significant effect on the stability of Y_2O_3 in $\text{H}_2 + \text{H}_2\text{O}$ environments.

Stability of CaO

Calculations show that Ca(g) is the primary reaction product for CaO in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres. The reaction can be written as



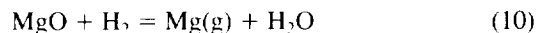
The equilibrium partial pressure of Ca(g) can be calculated from the expression

$$\log(p_{\text{Ca}}) = \log(K_8) + \log\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) \quad (9)$$

The calculated equilibrium partial pressures of Ca(g) as a function of moisture content and temperature are shown in figure 28 for 1-atm total pressure. The equilibrium partial pressure of Ca(g) increases with increasing temperature and decreases with increasing moisture content. The total system pressure has no significant effect on the equilibrium partial pressure of Ca.

Stability of MgO

Calculations show that Mg(g) is the predominant reaction product for MgO in $\text{H}_2 + \text{H}_2\text{O}$ environments. The relevant reaction is



The equilibrium partial pressure of Mg(g) can be calculated from the expression

$$\log(p_{\text{Mg}}) = \log(K_{10}) + \log\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}\right) \quad (11)$$

The equilibrium partial pressures of Mg(g) as a function of moisture content and temperature are shown in figure 29 for 1-atm total pressure. The partial pressure of Mg increases with increasing temperature and decreases with increasing moisture content. The total system pressure has no significant effect on the stability of MgO in $\text{H}_2 + \text{H}_2\text{O}$ environments.

Stability of BeO

The gaseous reaction products in either H_2 or $\text{H}_2 + \text{H}_2\text{O}$ atmospheres are BeOH(g) and Be(g) . The equilibrium partial

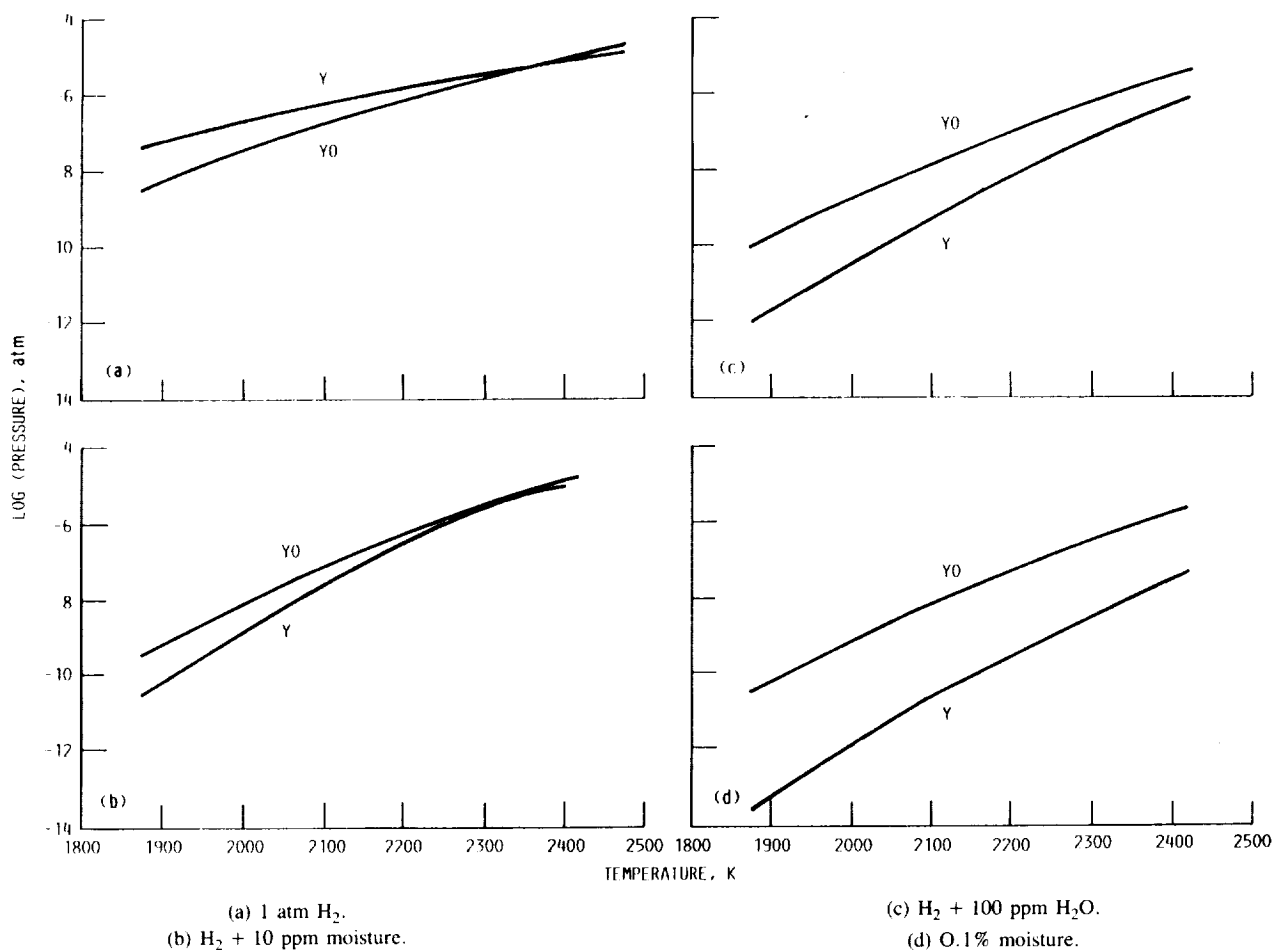


Figure 27.—Equilibrium partial pressures of Y(g) and YO(g) as a function of temperature and moisture content for reaction of Y_2O_3 with H_2/H_2O environments for 1 atm total pressure.

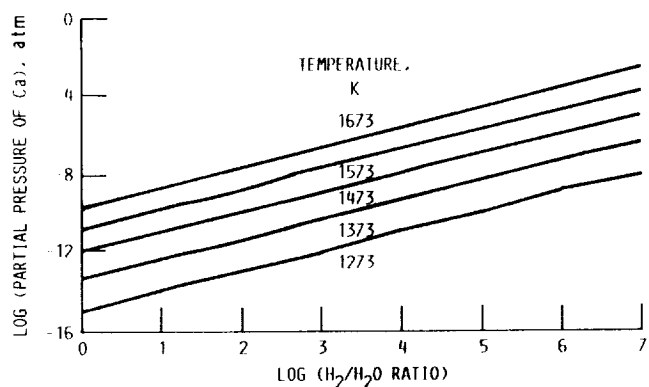


Figure 28.—Partial pressure of Ca(g) as a function of moisture content and temperature for reaction of CaO with $H_2 + H_2O$ atmospheres for a total pressure of 1 atm.

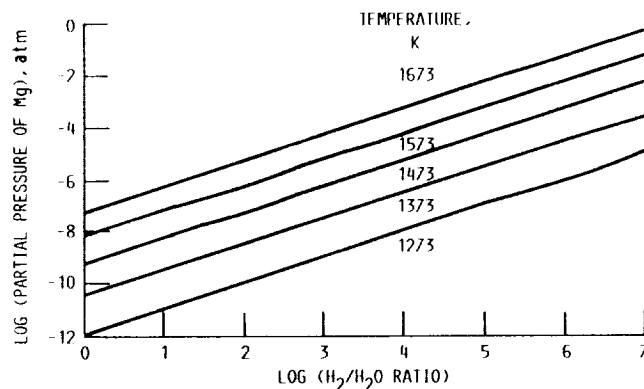


Figure 29.—Partial pressure of Mg(g) as a function of moisture content and temperature for reaction of MgO with $H_2 + H_2O$ atmospheres for a total pressure of 1 atm.

pressure of BeOH(g) is a few orders of magnitude higher than that of Be(g) , as shown in figure 30. It is interesting to note that the equilibrium partial pressure of BeOH(g) does not change with moisture content for the range of moisture levels considered in this study, specifically in the range 1 ppm to 50 percent. The equilibrium partial pressure of BeOH(g) increases with increasing temperature, as shown in figure 31. An increase in the total system pressure increases the equilibrium partial pressure of BeOH(g) , as shown in figure 32.

Stability of TiB_2

Stability in Pure H_2

The only stable solid phase in pure H_2 is TiB_2 . The gaseous reaction products are BH(g) and Ti(g) , the partial pressures of which, as a function of temperature, are shown in figure 33. The equilibrium partial pressures of these two gaseous species are marginally affected by the total system pressure as shown in figure 34.

Stability in $\text{H}_2 + \text{H}_2\text{O}$ Atmospheres

Figure 35 shows the stability of TiB_2 in $\text{H}_2 + \text{H}_2\text{O}$ environments at 2173 and 1673 K. At 2173 K, TiB_2 is the only stable solid phase for low moisture contents (< 100 ppm); TiB_2 and TiO are the stable solid phases for moisture contents greater than 100 ppm. Three stability regimes are evident at 1673 K. These are (1) $\text{TiB}_2 + \text{TiO}$ for moisture levels from 1 ppm to 0.25 percent, (2) $\text{TiB}_2 + \text{TiO}_2$ for moisture levels from 0.25 to 0.56 percent, and (3) $\text{TiB}_2 + \text{TiO}_2 + \text{B}_2\text{O}_3$ for moisture levels greater than 0.56 percent.

Formation of $\text{B}_2\text{O}_3(\text{l})$ is clearly detrimental to the oxidation resistance of TiB_2 in moisture-containing environments and is not desirable. Figure 36 gives the moisture level required for $\text{B}_2\text{O}_3(\text{l})$ formation as a function of temperature for 1-atm total pressure. The shaded portion of the figure denotes the region where $\text{B}_2\text{O}_3(\text{l})$ can be formed. The amount of moisture required for $\text{B}_2\text{O}_3(\text{l})$ formation increases with increasing temperature. At low temperatures such as 1173 K, the $\text{B}_2\text{O}_3(\text{l})$ can thus be formed at only 20-ppm moisture; the corresponding moisture level required at 1873 K is on the order of 6 percent.

The vapor pressure of $\text{B}_2\text{O}_3(\text{l})$ is quite high at high temperatures as shown in figure 37. For example, the equilibrium vapor pressure of B_2O_3 at 1673 K is on the order of 10^{-3} atm, which is quite high. In a dynamic environment, it is thus likely that $\text{B}_2\text{O}_3(\text{l})$ would instantly evaporate at this temperature, allowing a protective oxide layer to be developed. However, this may not be the case at lower temperatures, where the vapor pressure of $\text{B}_2\text{O}_3(\text{l})$ is low. This suggests that at lower temperatures TiB_2 may not be suitable for use in moisture-containing environments.

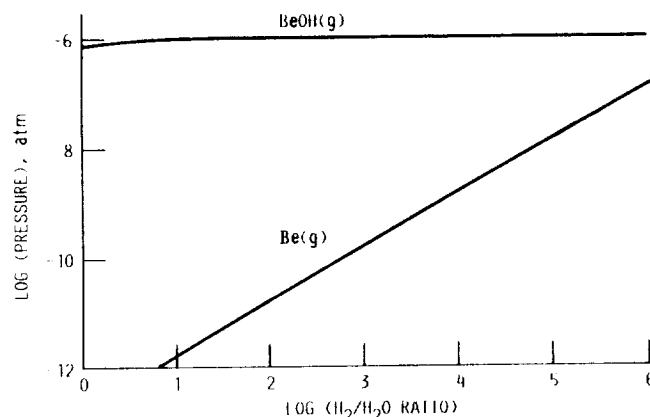


Figure 30.—Stability of BeO in $\text{H}_2 + \text{H}_2\text{O}$ atmospheres at 1673 K for a total pressure of 1 atm.

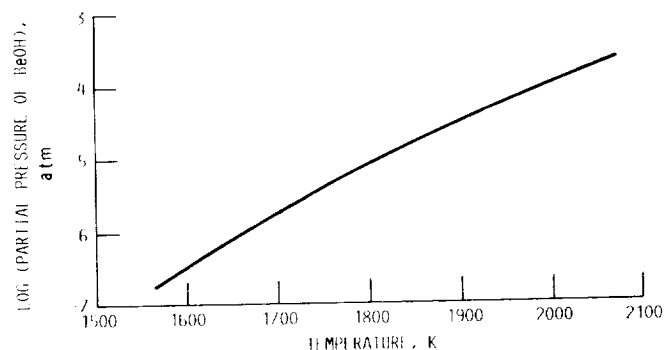


Figure 31.—Equilibrium partial pressure of BeOH(g) as a function of temperature for reaction of BeO with $\text{H}_2 + 100$ ppm H_2O environments for a total pressure of 1 atm.

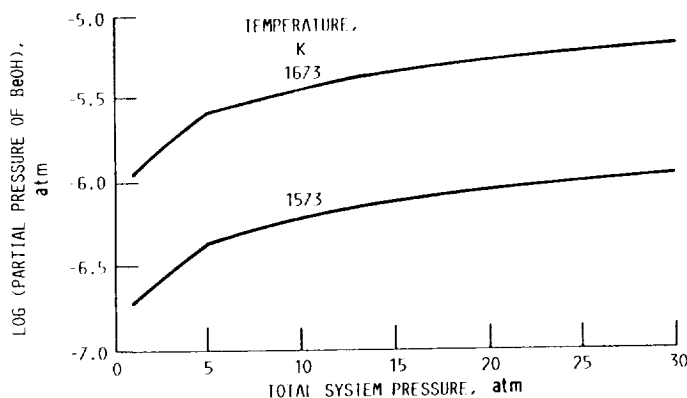


Figure 32.—Effect of total pressure on partial pressure of BeOH(g) for reaction of BeO with $\text{H}_2 + \text{H}_2\text{O}$ atmospheres.

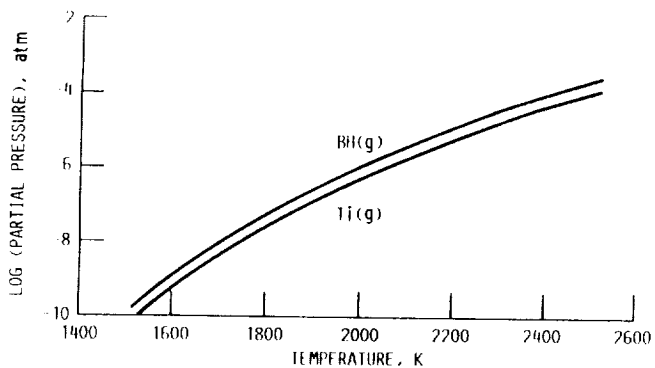


Figure 33.—Equilibrium partial pressures of BH(g) and Ti(g) as a function of temperature for reaction of TiB_2 with pure H_2 for a total pressure of 1 atm.

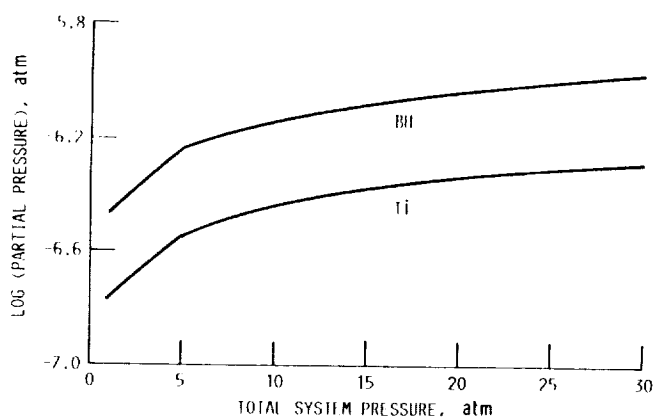


Figure 34.—Effect of total system pressure on the equilibrium partial pressure of BH(g) and Ti(g) for reaction of TiB_2 with pure H_2 at 1873 K.

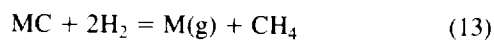
The total system pressure has marginal effect on the moisture levels required for $\text{B}_2\text{O}_3(\text{l})$ formation in the $\text{TiB}_2\text{-H}_2\text{-H}_2\text{O}$ system, as shown in figure 38.

Stability of TiC, ZrC, and HfC

At lower temperatures, the reaction of MC ($\text{M} = \text{Ti}, \text{Zr}, \text{or Hf}$) with H_2 results in the formation of M and CH_4 by the reaction



However, at higher temperatures, the gaseous M species becomes important and the reaction of MC with H_2 occurs via



Thus, MC and M are the stable condensed phases at lower temperatures, whereas MC is the only stable condensed phase at higher temperatures. The temperatures corresponding to the

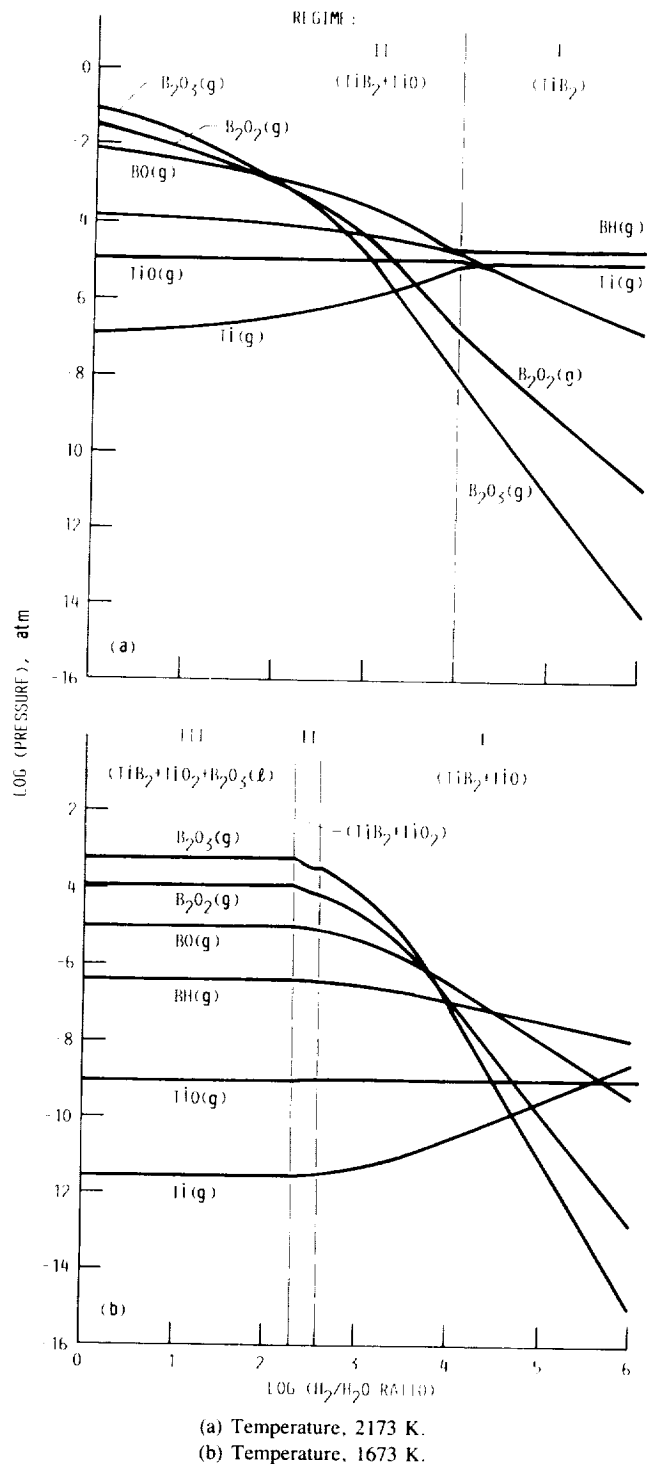


Figure 35.—Stability of TiB_2 in $\text{H}_2/\text{H}_2\text{O}$ environments for a total pressure of 1 atm.

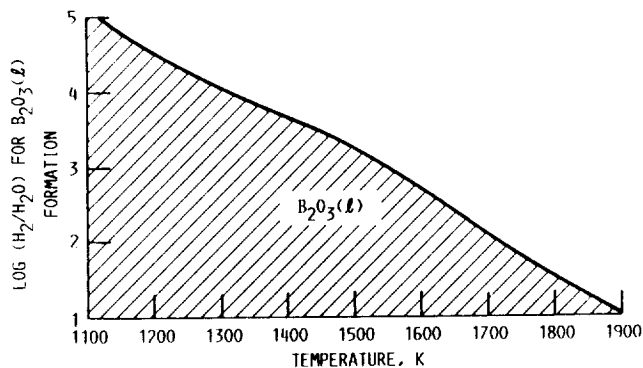


Figure 36.—Moisture content required for $B_2O_3(l)$ formation in $TiB_2-H_2-H_2O$ system as a function of temperature for a total pressure of 1 atm.

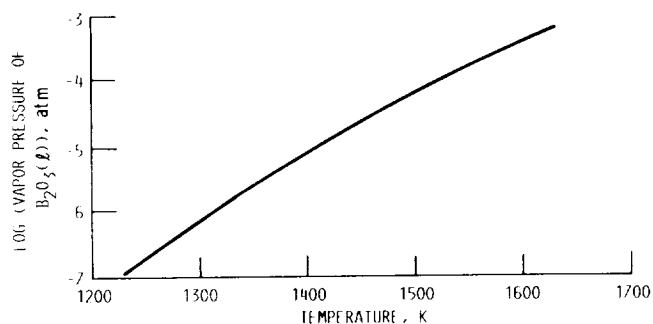


Figure 37.—Vapor pressure of $B_2O_3(l)$ as a function of temperature.

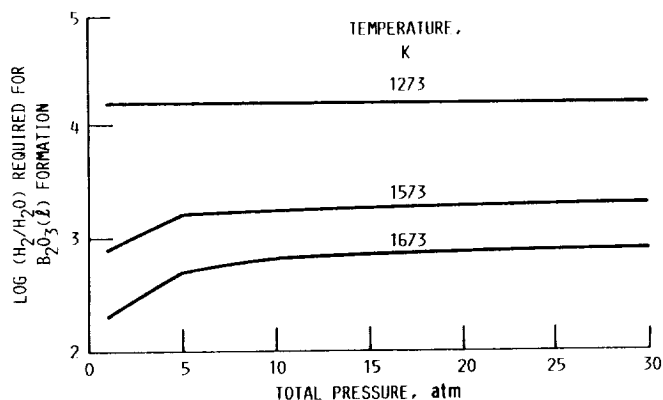


Figure 38.—Effect of total pressure on moisture content required for $B_2O_3(l)$ formation in $TiB_2-H_2-H_2O$ system.

transition from two stable condensed phases (MC + M) to one condensed phase (MC) are ~ 1573 K for TiC, ~ 2073 K for ZrC, and ~ 1873 K for HfC.

The total pressures of the product gases as a function of temperature for three MC- H_2 systems are shown in figure 39. The inflection points in the pressure-versus-temperature curves correspond to the temperature above which MC is the only stable condensed species. The total pressure of the product gases is the sum of the partial pressures of $CH_4(g)$ and $M(g)$.

An increase in the total system pressure raises the temperature corresponding to the transition from two stable condensed phases (MC + M) to one condensed phase (MC). For example, at 10-atm total pressure, the transition temperature for the TiC- H_2 equilibria is ~ 1973 K, as compared with 1573 K for 1-atm total pressure. The transition temperature for the ZrC- H_2 equilibria similarly increases from ~ 2073 to ~ 2873 K as the total system pressure is increased from 1 to 10 atm.

The oxides formed on TiC, ZrC, and HfC in moisture-containing environments are TiO , ZrO_2 , and HfO_2 , respectively. The stability of these three carbides in moisture-containing environments would thus depend on the protectiveness of these oxides.

Upper Temperature Limit for Different Ceramic Materials

One of the important objectives of thermodynamic calculations is to estimate an upper temperature limit for effective use of the ceramic materials in a given environment. Gaseous products are formed from the reaction of ceramic materials in a hydrogen-containing environment; the lower the equilibrium partial pressures for the reaction products, the longer will be the life of the component. Of course, kinetic factors must be considered in determining the long-term stability of a given material. However, in the absence of kinetic information, some guidelines on the upper temperature limit for a given material can be obtained if a maximum limit is defined for the total pressure of the reaction product gases above which the material may not be suitable for long-term use. It is probably reasonable to assume that the total pressure of reaction product gases less than 10^{-6} atm (1 ppm) would pose no long-term serious problems with respect to the degradation of a structural material. On the basis of this assumption, the upper temperature limits for different ceramic materials in H_2 and $H_2 + H_2O$ environments are shown in figures 40 and 41.

The upper temperature limit for SiC in pure H_2 is not shown because the equilibrium partial pressure of CH_4 for reaction (1) is greater than 10^{-6} atm at all temperatures. In view of the fact that both SiC and Si_3N_4 depend on a SiO_2 scale for protection against oxidation, the upper temperature limits for these two materials in $H_2 + H_2O$ environments correspond to the stability of SiO_2 . The stability of TiC,

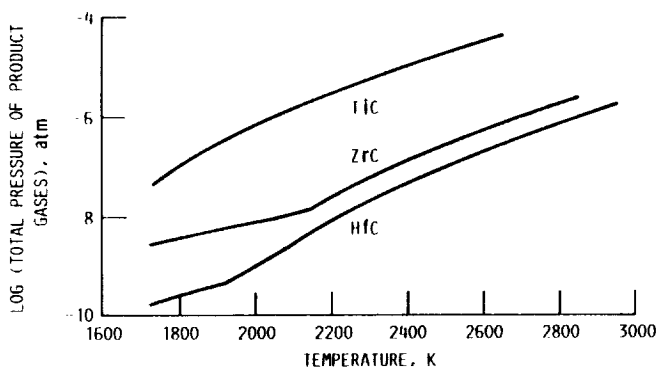


Figure 39.—Total pressure of product gases as a function of temperature for reaction of MC (M = Ti, Zr, or Hf) with pure H_2 for a total pressure of 1 atm.

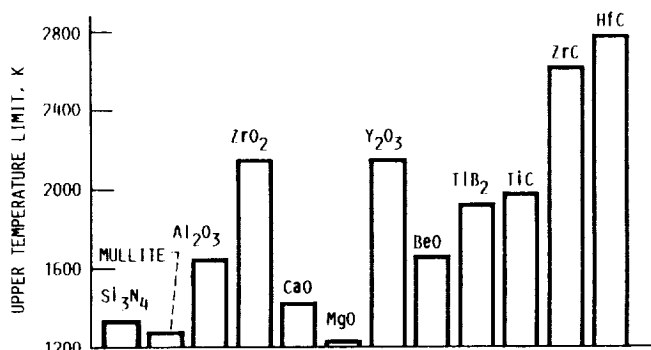


Figure 40.—Upper temperature limits for different ceramic materials in pure H_2 for a total pressure of 1 atm.

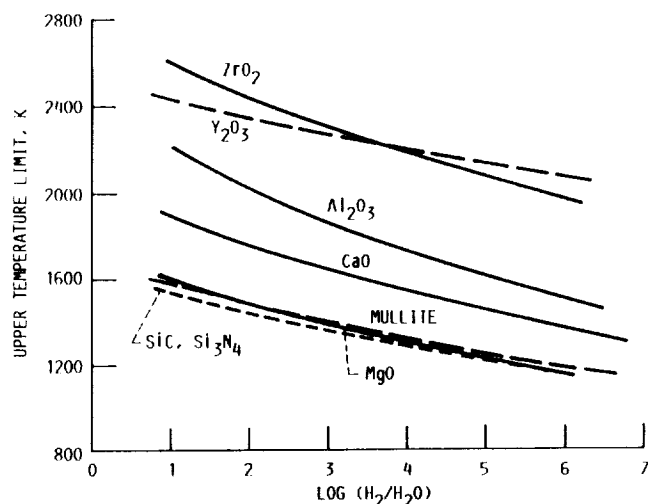


Figure 41.—Upper temperature limits for different ceramic materials in H_2/H_2O environments for a total pressure of 1 atm.

TiB_2 , HfC , and ZrC in $H_2 + H_2O$ environments would depend on the protectiveness of oxides such as TiO , TiO_2 , HfO_2 , and ZrO_2 . Because the oxides TiO_2 , ZrO_2 , and HfO_2 do not provide adequate protection during the oxidation of Ti, Zr, and Hf (ref. 11), the ability of these oxides to provide oxidation protection for the carbides and borides is rather questionable. No upper temperature limits are therefore defined for TiC , TiB_2 , HfC , and ZrC in $H_2 + H_2O$ environments.

The upper temperature limits for different ceramic materials in pure H_2 decrease in the following order: HfC , ZrC , ZrO_2 and Y_2O_3 , TiC , TiB_2 , BeO , Al_2O_3 , CaO , Si_3N_4 , mullite, and MgO . The compounds HfC , ZrC , TiC , and TiB_2 , although highly stable in pure H_2 , may not be suitable for moisture-containing environments.

The upper temperature limit for two common ceramic structural materials, SiC and Si_3N_4 , is only on the order of 1400 K for moderate moisture contents of about 100 ppm. The corresponding limit increases to about 1673 K for 10 percent moisture in the atmosphere.

Alumina can be used up to about 1640 K in pure H_2 and can be used at higher temperatures in moisture-containing environments. Zirconia is stable both in pure H_2 and $H_2 + H_2O$ atmospheres at very high temperatures. However, if CaO or MgO is used to stabilize ZrO_2 , the upper use temperature for ZrO_2 is considerably lowered. Thus, yttria-stabilized ZrO_2 should be preferred in H_2 -containing environments.

Concluding Remarks

The stability of several ceramic materials in H_2 and $H_2 + H_2O$ environments has been examined from thermochemical considerations, and the upper temperature limits have been defined for each ceramic material.

In conclusion, yttria-stabilized zirconia and alumina are the two ceramic materials that appear to be promising for long-term use in hydrogen-containing atmospheres at high temperatures (> 1673 K). The ceramic materials considered in this study are the ones currently being considered as possible structural materials either as monolithic materials or as constituents in ceramic-matrix composites. It is likely that there are other ceramic materials, especially the stable oxides such as La_2O_3 and Sc_2O_3 , that would also be stable in hydrogen-containing environments at elevated temperatures.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, August 28, 1989

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16. Abstract The chemical stability of several ceramic materials in hydrogen-containing environments has been analyzed with thermodynamic considerations in mind. Equilibrium calculations were made as a function of temperature, moisture content, and total system pressure. The following ceramic materials were considered in this study: SiC, Si ₃ N ₄ , SiO ₂ , Al ₂ O ₃ , mullite, ZrO ₂ , Y ₂ O ₃ , CaO, MgO, BeO, TiB ₂ , TiC, HfC, and ZrC. On the basis of purely thermodynamic arguments, upper temperature limits are suggested for each material for long-term use in H ₂ -containing atmospheres.					
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